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LXXIV.—RESEARCHES ON THE SODIUM SALTS OF THE AMIDES.

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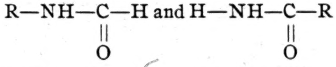
The work described in this paper was undertaken with the object of determining the relative ease with which certain acid amides yield sodium salts, and of determining whether a stereochemical interference is noticeable in this series, by comparing the velocity at which, under given conditions, metameric amides of the form $\mathrm{R{-}NH{-}}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{{-}H}$ and $\mathrm{H{-}NH{-}}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{{-}R}$ form salts. Such a comparison, taken in connection with a similar examination of the disubstituted formamides,



RNHCOR′ and R′NHCOR,

in which R = aryl and R′ = alphyl, might be expected to throw new light on the disputed question of the structure of these salts. For example, which one of the above-mentioned isomeric forms is most favorable for the formation of sodium salts, or in other words, in what position does R have the more retarding effect? And is this effect general for one of these types? If the sodium attaches itself to nitrogen, then R should exert a greater interference when attached to the same atom than when further removed or attached to carbon ; for example, formanilide, C_6H_5NHCOH, should then give a salt less easily than benzamide, $HNH—COC_6H_5$.

As regards the velocity of formation of the salts, the question of relative acidity or negative character of the molecules arises at once. Do the amides give salts in accordance with the strength of the acids from which they are derived ? To what extent does the basic character of the amino group influence the velocity of formation of the salts ?[1] The latter questions are evidently the first to be decided.

It was necessary at the outset to devise a new method for the preparation of the sodium salts. It was found that sodium amalgam answers the purpose better than metallic sodium ; that in boiling benzene the former does not become covered with a coating, as the metal does ; and that salts can be prepared by its use which cannot be obtained by any of the previously existing methods.

In order to determine whether acidity is the chief factor in determining the velocity of formation of the sodium salts, the following anilides in molecular proportions, taking 0.5 gram of acetanilide, were dissolved in 100 cc. of benzene and boiled for one hour with 9 grams of a 4.7 per cent amalgam. The solutions were then filtered as rapidly as possible, and the amount of anilide which had formed sodium salt was determined as described below. The following figures approximately show this amount in percentages, the affinity constants of the respective acids being given for comparison :

	Average of two experiments.		K.[2]
Formanilide, C_6H_5NHCHO,	1.00	Formic acid,	0.0214
Acetanilide, $C_6H_5NHCOCH_3$,	82	Acetic "	0.0018
Oxanilide, $(C_6H_5NHCO—)_2$,	63	Oxanilic "	1.21
Benzanilide, $C_6H_5NHCOC_6H_5$,	38	Benzoic "	0.006

From this it is evident that the results do not correspond with the strengths of the acids. Thus, oxanilide should give a salt more readily than formanilide and acetanilide, and benzanilide more readily than acetanilide.

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[1] It is well known that the presence of negative groups in the amides favors the formation of salts, dibenzamide, benzoylurethane, etc., are soluble in alkali, while benzamide is insoluble, and again, the acyl cyanamides have stronger acid properties than the acids from which they are derived. Bader : Ztschr. phys. Chem., **6**, 305.

[2] Ostwald : *Ibid.*, **3**, 241.

That basicity does not exert the most important influence, the acyl radical being the same, is shown by the following results, which were obtained under the same conditions :

Benzamide, $H_2NCOC_6H_5$,	98
Benzanilide, $C_6H_5HNCOC_6H_5$,	38
Benzoylbenzylamine, $C_6H_5CH_2HNCOC_6H_5$,	1

	K.[1]
Ammonia,	0.0023
Benzylamine,	0.0024

Thus, if the positive character of the molecules determined the velocity of formation of the salts, benzanilide should react more readily than benzamide ; and since benzylamine has practically the same basicity as ammonia, the benzoyl compounds should give salts with equal readiness.

It is interesting to note here that Hjelt[2] found that the rate of saponification of the alkyl malonic esters is not in agreement with the affinity constants of the corresponding acids, but that it agrees, rather, with what would be expected from the theory of stereochemical interference.

In order to determine which one of the two general forms, RNHCOH or HNHCOR, is more favorable for salt formation, the following amides were examined under the same conditions as described above, except that 23 grams of a 0.73 per cent amalgam were used. The figures represent the percentages of amide converted into sodium salt under these conditions :

	Average.
Formanilide, $C_6H_5.NHCO.H$,	57
Acetanilide, $C_6H_5.NHCO.CH_3$,	8
Propionanilide, $C_6H_5.NHCO.C_2H_5$,	12
Benzamide, $H.NHCO.C_6H_5$	51
Methylbenzamide, $CH_3.NHCO.C_6H_5$,	0
Ethylbenzamide, $C_2H_5.NHCO.C_6H_5$,	0

In the following cases the conditions were the same as in the first experiments, using a 4.7 per cent amalgam. In all cases excepting formanilide and benzamide, however, 150 cc. of benzene were used :

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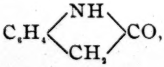
[1] Bredig : Ztschr. phys. Chem., **13**, 306.

[2] Ber. d. chem. Ges., **29**, 1866.

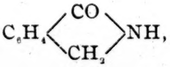
	Average.
Formanilide, C_6H_5NHCOH,	100
Orthoformtoluide, $C_6H_4CH_3NHCOH$,	96
α-Formnaphthalide, $C_{10}H_7.NHCOH$,	99
2,4,6-Trimethylformanilide, $C_6H_2(C_6H_3)_3NHCOH$,	96
Benzamide, $HNHCOC_6H_5$,	98
Orthotoluamide, $HNHCOC_6H_4CH_3$,	91
α-Naphthamide, $HNHCOC_{10}H_7$,	76
2,4,6-Trimethylbenzamide, $HNHCOC_6H_2(CH_3)_3$,	88

These results, thus far, show that a disubstituted formamide gives a salt less readily than one that is monosubstituted, which would be expected from the theory of stereochemical interference; and that when the larger or interfering radical is attached to nitrogen it has less effect in retarding the formation of sodium salts than when attached to the keto group. They, therefore, indicate that the sodium is attached to oxygen.[1] Although it is true that the results all point in this direction, nevertheless the interference which might be expected in certain cases does not exist, while in others an unexpected inertness is shown. An examination of the isomeric cycloamides, oxindol (I) and phthalimidine (II), under the same conditions as in the first experiments, showed that in both cases the amount of amide which had formed salt was practically 100 per cent, while benzoylbenzylamine (III), which has an acyclic structure corresponding to phthalimidine, as already stated, gave practically no salt under these conditions :



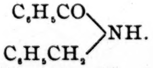
$C_6H_4\left\langle {NH \atop CH_2} \right\rangle CO,$

I.



$C_6H_4\left\langle {CO \atop CH_2} \right\rangle NH,$

II.



$\left. {C_6H_5CO \atop C_6H_5CH_2} \right\rangle NH.$

III.

The interesting results obtained by Remsen and Reid[2] on the saponification of the substituted benzamides show that substituents in the ortho position "exert a remarkable protective influence on the amide group." The order in which the various groups produce a retardation was found to be as follows, in order of decreasing influence: —NO_2, —I, —NH_2, —CH_3, —Cl, —OH, —$O.C_2H_5$, —$O.CH_3$. Unfortunately, for a comparison with the velocity of formation of the corresponding sodium salts, only —NH_2, —CH_3, and the least interfering groups, —$O.C_2H_5$ and —$O.CH_3$, are probably available for examination by the present method. The results with orthotoluamide indicate, however, that interference also plays a part in the formation of the sodium salt of that compound, although it is not shown in a very decided manner. On the other hand, it is curious that benzoylbenzylamine, and methyl- and ethylbenzamides are so inert, and that they give salts less readily than benzanilide, while the results with trimethylbenzamide are most unexpectedly high.

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[1] Compare Michael : J. prakt. Chem., **60**, 322.

[2] This JOURNAL, **21**, 281.

The derivatives of 2-4-6-trimethylbenzoic acid, like other diorthosubstituted acids, are notably inactive in reactions which are supposed to involve an addition to the keto group.[1] The acid is not converted into its ester by means of hydrogen chloride and alcohol.[2] The ester[3] and amide[4] are difficult to saponify, while the chloride is remarkably stable towards water and alkalies. Diorthosubstituted acid chlorides in general react readily with ammonia,[5] however, and the silver salt of trimethylbenzoic acid gives almost a quantitative yield of the ester with methyl iodide.[6] It is assumed that these latter reactions do not involve any addition to the keto group, but take place by direct substitution.[7] The fact now that 2,4,6-trimethylbenzamide forms a sodium salt practically as readily as orthotoluamide, and that no very decided stereochemical interference is found in this reaction, would suggest that here, also, direct substitution takes place, and that the sodium is attached to nitrogen. On the other hand, if the sodium is attached to oxygen, the reaction must be an addition of sodium hydrate to the keto group, and then a separation of water, as follows:[1]

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[1] Henry: Ber. d. chem. Ges., **10**, 2041; Wegscheider: Monatshefte, **16**, 148; Angeli: Ber. d. chem. Ges., **29**, R, 591; Peckmann; *Ibid.*, **31**, 504.

[2] V. Meyer: *Ibid.*, **27**, 510.

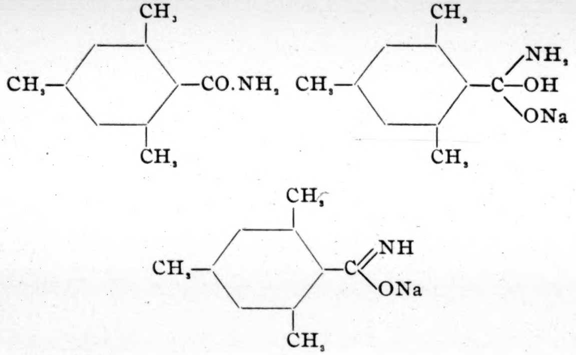
[3] *Ibid.*, **27**, 1263.

[4] Sudborough: J. Chem. Soc. (London), 1897, 229.

[5] Sudborough: *Ibid.*, 1897, 234.

[6] Meyer: Ber. d. chem. Ges., **27**, 1580.

[7] Max Scholtz: Der Einfluss d. Raumerfüllung d. Atomgruppen; Sudborough: *Loc. cit.*



If this is true, it follows that 2,4,6-trimethylbenzamide, out of all harmony with the theory of stereochemical interference, must readily form an addition-product with the alkali. This is precisely what takes place, not only in this case but also with the symmetrical 2,4,6-tribrombenzamide, which Sudborough states exhibits the greatest amount of stereochemical interference, as regards its hydrolysis, of any of the amides examined by him.

The ease with which 2,4,6-trimethylbenzamide forms a sodium salt is therefore in harmony with the theory that the metal in the sodium salts of the amides is attached to oxygen.

I have found that 2,4,6-trimethyl- and tribrombenzamides are readily removed from even their dilute solutions in ether by simply shaking with powdered potassium hydrate, the addition-product being absolutely insoluble in ether. On filtering and treating the residue with water, these compounds undergo dissociation and the unaltered amides are recovered.

In order to prepare the compound $C_6H_2Br_3CONH_2.NaOH$, it is simply necessary to pour an excess of the amide dissolved in benzene over finely powdered sodium hydrate, whereupon the latter is quantitatively converted into the addition-product.[1]

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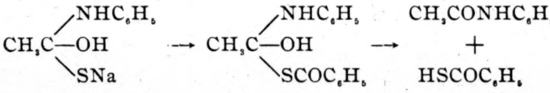
[1] Naturally a mere trace of moisture would be sufficient, since the water which separates would again react until all the amide is converted by the sodium into salt.

This is all the more surprising since Pechmann[2] found that 2,4,6-trimethylbenzoic ester does not form an addition-product with sodium alcoholate, which is one of the notable properties of ethyl benzoate, and I have found that 2,4,6-tribrombenzoyl chloride and methyl 2,4,6-tribrombenzoate do not give addition-products with potassium hydrate, and also that 2,4,6-tribrom-N-dimethylbenzamide yields no sodium hydrate compound under the same conditions that proved successful with the amide.

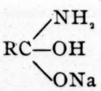
The readiness with which the diorthosubstituted amides form addition-products with the alkali, contrasted with their inertness as regards saponification, suggests that the processes involved in the formation of sodium salts and in saponification are not analogous. If we accept the addition theory of saponification the existence of these alkali addition-products shows that the stereochemical interference in regard to the saponification of these amides, at least with alkali, is not due to a protection from attack, but, for some other specific reason, they give up ammonia with difficulty.

That these alkali addition-products have the elements of the alkali attached to the keto group, and are not merely so-called molecular compounds, is shown by the behavior of the sodium hydrate addition-product of thioacetanilide with benzoyl chloride, which reaction yields acetanilide and thiobenzoic acid, as follows:



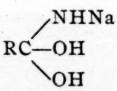
$$\mathrm{CH_3C}\begin{array}{l}\diagup \mathrm{NHC_6H_5}\\ \!-\mathrm{OH}\\ \diagdown \mathrm{SNa}\end{array} \longrightarrow \mathrm{CH_3C}\begin{array}{l}\diagup \mathrm{NHC_6H_5}\\ \!-\mathrm{OH}\\ \diagdown \mathrm{SCOC_6H_5}\end{array} \longrightarrow \begin{array}{c}\mathrm{CH_3CONHC_6H_5}\\ +\\ \mathrm{HSCOC_6H_5}\end{array}$$

That they have the formula



$$\mathrm{RC}\begin{array}{l}\diagup \mathrm{NH_2}\\ \!-\mathrm{OH}\\ \diagdown \mathrm{ONa}\end{array}$$

and not



$$\mathrm{RC}\begin{array}{l}\diagup \mathrm{NHNa}\\ \!-\mathrm{OH}\\ \diagdown \mathrm{OH}\end{array}$$

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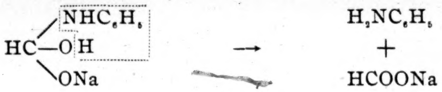
[1] Interesting also, in this connection, is the fact that Küster and Stallberg (Ann. Chem. (Liebig), **278**, 217) state that 3-nitro-2,4,6-trimethylbenzamide dissolves in aqueous alkali and even in carbonates.

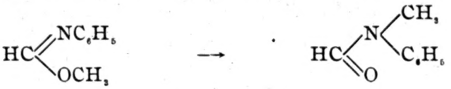
[2] *Loc. cit.*

is shown by the behavior[1] of the addition-products of formanilide, formtoluide, etc.

When heated, or, as found by Tobias,[2] when simply allowed to stand over sulphuric acid, these compounds decompose as follows:



This formula, as representing the structure of these addition-products is objected to by Cohen and Brittain,[3] since when heated the analogous sodium alcoholate addition-products[4] lose alcohol and yield sodium[5] acetanilide, which, with methyl iodide, gives methylacetanilide, methylaniline, etc. Their statement that this formula "would necessitate a molecular change of a very complex character which is scarcely justified by the facts" no longer holds true, since phenylformimidomethyl ester undergoes this rearrangement with methyl iodide, even in the cold, yielding methylacetanilide:



EXPERIMENTAL PART.

Experiments with a 0.73 Per Cent Amalgam.

Formanilide.—The method adopted in general for the determination of the ease with which the amides form salts was as follows: 0.4481 of a gram of formanilide and the equivalent of the other amides were dissolved in 100 cc. of benzene and heated, whereupon 23 grams of a 0.73 per cent amalgam were added. This is somewhat more than twice the calculated quantity of sodium. After boiling one hour, the solution was filtered and the residue of sodium salt was collected on the filter, while the heavier amalgam was allowed to remain in the flask.

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[1] See also Hantzsch: Ann. Chem. (Liebig), **296**, 91.

[2] Ber. d. chem. Ges., **15**, 2451.

[3] J. Chem. Soc. (London), 1898, 162.

[4] Cohen and Archdeacon: *Ibid.*, **69**, 91.

[5] Seifert: Ber. d. chem. Ges., **18**, 1358.

The whole was washed with somewhat over 50 cc. of warm benzene by means of a wash-bottle and the filtrate evaporated in a weighed flask, the residue being dried in a stream of air at ordinary temperature. In most cases the residue consisted of unaltered amide, which gave directly the weight of material not forming sodium salt. In all cases this residue, after weighing, was treated with water and titrated with a standard hydrochloric acid solution, using an aqueous solution of the sodium salt of orthonitrophenol as indicator, which recommended itself, since it gives a very sharp end-reaction by gaslight and carbonic acid does not interfere except in the cold.

In this manner the amount of sodium salt dissolved by the benzene was determined and the correction made. The amount of amide forming sodium salt was then determined by difference. In some of the experiments the amount of anilide recovered, after boiling with amalgam, was determined by saponifying the anilide with strong hydrochloric acid and then determining the amount of aniline volumetrically by means of a standardized solution of potassium bromate and bromide.[1]

Two experiments with formanilide, performed as above, gave 0.1963 and 0.1859 gram anilide not attacked, corresponding to 56 and 58 per cent as sodium salt. This sodium salt is insoluble in benzene.

It must be understood that the quantitative results given in this paper are merely approximate, and in certain cases it is difficult to get closely agreeing results. The first difficulty encountered is the fact that with the solid amalgam it is difficult to get the same state of division each time, although in each case the amalgam was freshly powdered and passed through a moderately fine sieve before it was used. A curious result was observed when two different preparations of a semisolid amalgam was used, both containing the same percentage of sodium as far as could be determined; *i. e.* 0.72 and 0.73 per cent. By means of the latter, when acetanilide was boiled for one hour, 8.7 and 8.0 per cent was found to have been converted into sodium salt; with the former preparation, however, on boiling for two hours three experiments each gave

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[1] Reinhardt: Ztschr. anal. Chem., **33**, 90; Compare Francois and Denigès: J. Soc. Chem. Ind., **28**, 866.

3.9 per cent as the amount of anilide that had been attacked.

It has previously been observed that certain preparations of sodium amalgam have given widely different results in reduction experiments[1] and Aschan [2]explains this by the assumption that impurities cause the evolution of hydrogen in the molecular form and not in an active state. This explanation fails in the above case. With these results, which fortunately occurred at the beginning of the work, all the comparisons were afterwards made with portions of the same preparations.

Other sources of error are as follows: The sodium salts are bulky, gelatinous, and difficult to wash when prepared in this way; therefore, the small quantities of amides used in the experiments, and, in some cases, the residues left on evaporating the benzene, are difficult to dry. In no case was any reduction of the amide observed, as is the case when the amides are acted on with amalgam in acid[3] or alkaline[4] solutions.

Acetanilide.—When two experiments with 0.5 gram of this anilide were performed as described above, 8.7 and 7.9 per cent of the anilide was found to have been converted into sodium salt. This quantity was all dissolved in the benzene solution. Experiments at 20°, the other conditions being exactly the same, gave peculiar results. It was found that 17.8 and 20.8 per cent of the acetanilide had been converted into sodium compound, or about two and one-half times as much as at the temperature of boiling benzene. The explanation of this was found on filtering the benzene solution, when before the washing was complete the sodium hydrate addition-product mentioned by Cohen and Brittain[5] began to separate. This owed its formation to the unavoidable presence of moisture absorbed by the amalgam and benzene during the manipulation. These authors state that the alkali addition-products are readily dissociated at the temperature of boiling ether; therefore, all other experiments described here were performed at the temperature of boiling benzene.

The sodium hydrate addition-product of acetanilide is soluble in benzene, while that of formanilide is insoluble ; therefore, at temperatures at which the intermediate addition-products are stable, more sodium compound should be formed in the case of acetanilide than with formanilide, when treated with metallic sodium covered with a layer of sodium hydrate. The results of the following experiments proved this to be true. The anilides were dissolved in 100 cc. of benzene (0.4481 gram formanilide and 0.5 gram acetanilide) and shaken in a machine for one hour, with 0.5 gram of sodium, weighed in the air whereupon formanilide gave 5.3 and 5.9 per cent, and acetanilide 20.5 and 26.3 per cent anilide as sodium compound.

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[1] Lassar-Cohn: Lab. Manual Org. Chem., p. 308.

[2] Ber. d. chem. Ges., **24**, 1866.

[3] Guareschi: *Ibid.*, **7**, 1462.

[4] Hutchinson: *Ibid.*, **24**, 173.

[5] *Loc. cit.*

Propionanilide.—One experiment with 0.5518 gram of this anilide, which was performed in boiling benzene, gave no turbidity or separation of salt from the benzene solution, but on filtering and evaporating, 12.2 per cent was found to have been converted into salt.

Benzamide.—In this case two experiments with 0.4481 gram of material gave 1.4 per cent of amide as sodium compound dissolved in benzene and 49.1 and 50.2 undissolved ; total 50.5 and 51.6.

Methyl- and Ethylbenzamides gave no evidence of any salt formation under the above conditions. The benzene solution was found to be free from alkali and, on evaporating off the benzene, the weights of the residues came from 2 to 5 per cent too high, it being difficult to dry the material without loss.

Experiments with a 4.7 Per Cent Amalgam.

Formanilide.—In each of the following experiments 9 grams, or five times the calculated quantity of amalgam, was used. 0.4481 gram of this anilide, when treated as above, gave no residue on evaporating the benzene; hence the amount of salt formed was 100 per cent.

Acetanilide.—One-half gram gave, in two experiments, 29.6 per cent as salt dissolved in the benzene, and 48.1 per cent undissolved in one; and 29.6 and 56.8 per cent in another ; total 77.7 and 86.4 ; average 82. Lack of better agreement is due to the difficulty of drying, owing to the amount of salt dissolved by the benzene.

Oxanilide.—In two experiments 0.4444 gram gave 65.4 and 60.0 as monosodium salt. This salt is insoluble in benzene; it was separated from all but traces of the amalgam by decantation, and a sodium determination gave:

	Calculated for $C_6H_5NHCOCONaNC_6H_5$.	Found.
Na	8.8	9.1

Water decomposes the salt,[1] liberating anilide.

Benzanilide.—Attempts to prepare a sodium salt for synthetical purposes by boiling this anilide in benzene with sodium were unsuccessful. Quantitative experiments indicated that over 95 per cent of the anilide was unaltered. The use of xylene, as recommended by Hepp,[2] gave no better result. The method of Seifert[3] and Blacher[4] for the preparation of sodium salts also failed in this case. It was prepared, however, by boiling the concentrated benzene solution with an 8 per cent amalgam. Ten grams anilide gave about 7 grams of salt after boiling several hours. It was separated from the excess of amalgam by decantation. As the amalgam used was not freshly prepared and contained some sodium hydrate, the results on analysis came high. The percentage of sodium calculated is 10.5, found 11.7. In the experiments of Paal and Otten[5] on the action of acyl chloride on the sodium salts of the anilides, they invariably treated the salt of a lower anilide with a chloride of higher acid, benzoyl chloride with sodium acetanilide, sodium formanilide, etc., and obtained nothing but the anilide of the higher acid. The action proved to be abnormal as diacyl anilides were not obtained. It seemed of interest, therefore, to try the action of acetyl chloride on sodium benzanilide under the same conditions as described by the above authors, when it was found that the action was also abnormal in this case, and that nothing but benzanilide was obtained.

[1] In determining the amount of sodium in the following new salts, which was done volumetrically, a determination of the amount of mercury was also necessary in some cases: in others this was very small and was disregarded. The decanted precipitates always contain more or less mercury.

[2] Ber. d. chem. Ges., **10**, 328.

[3] *Ibid.*, **18**, 1357.

[4] *Ibid.*, **28**, 435.

[5] *Ibid.*, **23**, 2587.

Quantitative experiments with 0.7296 gram anilide, on the formation of sodium benzanilide, gave 35.3 as the amount of amide which had formed salt, in one, and 40.5 per cent in another; average, 37.9. The salt is insoluble in benzene; it is bulky and gelatinous, but when dried forms a white, amorphous powder.

Benzamide.—The amide (0.4481 gram) gave 98 per cent as the amount that had formed salt, while 1.4 per cent of the amide was in solution as sodium salt. After decanting the bulky, gelatinous salt and rapidly drying in a steam oven a sodium determination gave:

	Calculated for C_7H_6NONa.	Found.
Na	16.0	16.2

Ethylbenzamide.—Two experiments with 0.5518 gram each of this amide, again with the stronger amalgam, gave no evidence of any salt formation. On boiling the benzene solution it remained perfectly clear, and on examining the residue left on evaporating the benzene it was found that less than 0.7 per cent of the amide had formed salt.

Benzoylbenzylamine.—This was prepared by the Baumann-Schotten reaction. Two experiments with 0.7815 gram of material gave perfectly clear solutions on boiling with the amalgam, and an examination of the residue, on evaporating the benzene solution, indicated that in both cases 1.0 per cent of the amide had been converted into sodium salt. The recovered material melted sharply from 106° to 107°.

Oxindol.—This cycloamide (0.4926 gram) gave a bulky, gelatinous separation of salt immediately on warming and, on evaporating the filtered solution, the residue weighed 0.0050 gram. It was found to be free from alkali, and, therefore, 99 per cent of the amide was converted into salt. A sodium determination gave:

	Calculated for C_8H_6NONa.	Found.
Na	14.8	15.3

Phthalimidine.—This amide (0.4926 gram) gave a bulky, gelatinous salt, like the above, and the recovered residue of unaltered material weighed 0.0066 gram ; hence 98.7 per cent of the amide formed salt. A sodium determination gave :

	Calculated for C_8H_6NONa.	Found.
Na	14.8	14.8

Phenyloxamide.—This amide (0.3037 gram) refused to dissolve completely in 100 cc. of benzene before adding the amalgam, so that the results are not directly comparable with the above. The amount of amide converted into salt was found to be 57.3 per cent.

Oxamide and *phthalamide* are insoluble in benzene. *Formamide*[1] immediately liberates ammonia, while *acetamide* appears to be less readily decomposed by the above treatment.

The following experiments required the use of 150 cc. of benzene, owing to the difficulty with which α-naphthamide dissolves in this solvent.

Orthoformtoluide.—This was one of the few cases in which the amalgam showed any tendency to "cake," or the salt to attach itself to the amalgam ; nevertheless, 0.5 gram gave 95.7 per cent as the quantity of toluide forming sodium salt ; 3 per cent of this was dissolved by the benzene. The salt separated by decantation gave :

	Calculated for C_8H_8NONa.	Found.
Na	14.6	14.2

Orthotoluamide.—This was prepared by the method suggested by Remsen and Reid. The amount used was 0.5 gram, and 90.6 per cent of this was found to have formed sodium salt. No salt was found in the benzene solution. A sodium determination gave :

	Calculated for C_8H_8NONa.	Found.
Na	14.6	15.1

α-Formnaphthalide.—Of this, 0.6333 gram gave 98.9 per cent as sodium salt. It is bulky and gelatinous, and therefore filters slowly. Less than 1 per cent of salt was found in the benzene. A sodium determination gave :

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[1] That this amide gives a sodium salt with great ease, by a less energetic reaction, is shown by the method used by Freer and Sherman (This JOURNAL, **18**, 580).

	Calculated for $C_{11}H_8NONa$.	Found.
Na	11.8	12.2

α-Naphthamide.—The nitrile was prepared from α-naphthylamine by the Sandmeyer reaction. Of the amine 85.8 grams gave 13 grams of nitrile boiling at about 300°. When this was dissolved in an excess of alcoholic sodium hydrate and warmed for a few minutes, the first separation of crystals weighed 5 grams and were practically pure amide, melting at 202°.

The amide (0.6333 gram) gave 23.6 per cent unaltered material. After being heated as above, this melted sharply at 202°. The amount of amide as sodium salt was therefore 76.4 per cent. A sodium determination gave:

	Calculated for $C_{11}H_8NONa$.	Found.
Na	11.8	12.4

2,4,6-Trimethylformanilide.—The mesidine was prepared by heating trimethylphenylammonium iodide at 210° with a few drops of methyl alcohol. It is more readily obtained from mesitylene by nitration and reduction. The formyl compound melted at 177°. Of this, 0.6037 gram gave 95.9 per cent as sodium salt, which separated as a bulky, gelatinous mass. Less than 1 per cent of this was dissolved by the benzene. A sodium determination gave:

	Calculated for $C_{10}H_{12}NONa$.	Found.
Na	12.4	12.3

2,4,6-Trimethylbenzamide.—For the preparation of this amide mesitylene was nitrated according to the method of Schulz.[1] After distilling in steam, the oil obtained was distilled at 15–20 mm. pressure, when the fraction, 120°–130°, was collected. It boils for the most part at 150°–154° at about 50 mm. pressure. 131 grams of mesitylene gave 61 grams of crude nitro-compound. This, on reduction, gave 25.3 grams of mesidine boiling from 224°–226° (uncorr.). From this the nitrile was prepared according to Sandmeyer's reaction, using the conditions of Liebermann and Birukoff[2] for the preparation of the corresponding 2,4-xylylic nitrile. They obtained a yield of 50–60 per cent. In the present case the yield was far below this, about 8 grams of crude nitrile being obtained. On boiling this for seventy-two hours with alcoholic potash, the first separation of crystals, on cooling and crystallizing the product from benzene, weighed 2 grams and melted sharply from 187°–188°.

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[1] Ber. d. chem. Ges., **17**, 477.

[2] Ann. Chem. (Liebig), **240**, 286.

When 0.6037 gram of this amide was treated with the amalgam an immediate turbidity of the benzene solution resulted, and an extremely gelatinous precipitate separated which was difficult to wash. The salt is absolutely insoluble in benzene and 87.8 per cent of the amide was converted into salt. A sodium determination gave:

	Calculated for $C_{10}H_{12}NONa$.	Found.
Na	12.4	12.8

2,4,6-Trimethylbenzamide and Potassium Hydrate.—It was found that this amide readily unites with alkali in the following way: Potassium hydrate was used, as Cohen states that these addition-products, in the case of the substituted acetanilides, are more soluble than the sodium hydrate compounds. Of this amide 0.3003 gram was dissolved in 100 cc. of ether, in which it is readily soluble, and 2 grams of potassium hydrate were powdered under 40 cc. of ether and then the whole mixed together. The mixture was shaken for half an hour and then filtered into a weighed flask. It was washed with 100 cc. of ether and, on evaporating the ether and drying the residue in a stream of air for a few minutes, 0.0115 gram of unaltered amide was recovered; 96.2 per cent had, therefore, combined with the alkali. On treating the alkali with water the amide was recovered.

2,4,6-Tribrombenzamide.—This was prepared from metaminobenzoic acid. Tribrombenzoic acid was prepared by eliminating the amino group from this after brominating.[1] Twenty grams of aminobenzoic acid gave 52 grams of the tribromamino acid melting at 170°–172°, and this gave 43 grams of crude tribrombenzoic acid. This was converted into the chloride in the usual way, and, instead of attempting to purify this by crystallizing from petroleum ether, in which the compound is readily soluble, it was distilled[1] under a pressure of 35–40 mm., when the chloride boiled from 200°–210°. On cooling the distillate, beautiful, four-sided tables separated, melting at about 47°. These were crystallized from petroleum ether. The yield was 25 grams. The amide separated immediately when this material was dissolved in alcoholic ammonia, and it melted sharply from 191°–192°.

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[1] Volbrecht: Ber. d. chem. Ges., **10**, 1708.

This amide is the most difficult to saponify of any yet examined; nevertheless it unites with alkali to form addition-products with the greatest ease.

2,4,6-Tribrombenzamide and Potassium Hydrate.—1.0040 grams of the amide were dissolved in 100 cc. ether and 2 grams of potassium hydrate, powdered under 40 cc. of ether, were added. After shaking for half an hour the material was filtered and washed with 100 cc. of ether. On evaporating the filtrate only 0.0145 gram of residue was obtained. Therefore, 98.7 per cent of the amide had formed an addition-product with the alkali, and was filtered off.

2,4,6-Tribrombenzamide Sodium Hydrate, $C_6H_2Br_3CONH_2.NaOH$.—These addition-products can be isolated in a state of purity, as follows: 4 grams of the amide are dissolved in 150 cc. of benzene, and the solution poured on 0.3 gram of pure sodium hydrate in a mortar (calculated quantity 0.4 gram). The alkali is thoroughly powdered and then the mass is filtered and washed with benzene, in which the addition-product is insoluble. On drying rapidly in a steam-bath, a sample thus prepared gave the following result on determining sodium hydrate:

	Calculated for $C_6H_2Br_3CONH_2.NaOH$.	Found.
NaOH	10.0	10.3

Under the microscope the material appeared minutely crystalline, but no definite form could be observed. It was absolutely free from the characteristic needles of the free amide. Water immediately decomposes the compound.

2,4,6-Tribrom-N-dimethylbenzamide, $C_6H_2Br_3CO.N(CH_3)_2$.—This was prepared by treating the acid chloride with an excess of an aqueous 33 per cent solution of dimethylamine mixed with methyl alcohol. The product thus obtained was purified by crystallizing from a mixture of benzene and petroleum ether, whereupon well developed, colorless prisms separated melting from 85°–86°. A nitrogen determination gave:

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[1] Sudborough: *Loc. cit.*

	Calculated for $C_9H_8Br_3NO$.	Found.
N	3.61	3.57

When 2 grams of this amide were dissolved in 30 cc. of benzene and treated with 1.5 grams powdered sodium hydrate no addition took place. The alkali was free from amide, on filtering and washing, and the benzene solution contained no alkali.

2,4,6-Tribrombenzoyl Chloride and Potassium Hydrate.—1.1020 grams of the chloride were dissolved in 50 cc. of ether and 2 grams of potassium hydrate, powdered under 40 cc. of ether, were added. After twenty minutes the mixture was filtered, washed with 100 cc. of ether, and the ether evaporated, when the residue weighed 1.0620 grams. No alkali was found in this residue, hence 96.3 per cent of the chloride remained unaffected in this treatment.

2,4,6-Methyltribrombenzoate and Potassium Hydrate.—1.0055 grams of the ester were treated with 2 grams of powdered potassium hydrate, as above described, when 0.9841 gram of unaltered material was recovered, or 97.8 per cent.

Thioacetanilide Sodium Hydrate, $CH_3CS—NHC_6H_5.NaOH$.—1.2 grams of sodium hydrate (calculated 1.7) were powdered under a solution of 6.6 grams of thioacetanilide in 30 cc. of benzene. A finely divided precipitate formed at once, which was very slow in filtering. It was washed with a little ether and dried at about 55°, whereupon a sodium determination gave:

	Calculated for $C_8H_9NS.NaOH$.	Found.
Na	12.0	11.8

Thioacetanilide Sodium Hydrate and Benzoyl Chloride.—5.2 grams of the above were mixed with 3.5 grams of benzoyl chloride in 30 cc. of ether, whereupon reaction immediately set in with evolution of heat. On filtering and evaporating the ether a yellow oil was obtained, which, on standing over night, deposited a mass of needles or prisms. When these were washed with ether and crystallized from water broad, colorless plates of acetanilide were obtained melting at 114°. The yellow oil was easily recognized as thiobenzoic acid by its peculiar, disagreeable odor. It could not be distilled even under diminished pressure. When it was mixed with aniline in the cold it gave benzanilide.

The above sodium-hydrate addition-product appears to be formed when sodium alcoholate and thioacetanilide in alcohol are precipitated with moist ether. A portion prepared in this manner by Dr. P. T. Walden and treated with benzoyl chloride gave the same result as above. A determination of nitrogen in the crystals obtained proved that the material was acetanilide.

NEW HAVEN, CONN., February 28, 1900.

Contribution from the Division of Chemistry, U. S. Department of Agriculture.

ESTIMATION OF ALKALI CARBONATES IN THE PRESENCE OF BICARBONATES.

BY FRANK K. CAMERON.

Introduction.

In an aqueous solution sodium carbonate is hydrolyzed to a definite extent, depending upon the concentration and temperature conditions. This may be represented thus:

$$Na_2CO_3 + HOH \rightleftarrows NaHCO_3 + NaOH.$$

Of the four electrolytes then present in the solution only the sodium hydroxide is dissociated or ionized to any considerable extent, and in consequence the solution presents the characteristic features of a solution of this substance—it is markedly alkaline. Shields[1] has found the amount of this hydrolysis for a tenth-normal (N/10) solution of sodium carbonate at 25° C. to be about 3.17 per cent. For certain purposes it is desirable to determine the " alkalinity of such a solution, that is to say, the amount of sodium ions which may possibly result from this hydrolytic action, or one-half the sodium which has been brought into the solution as sodium carbonate. This may be done by titrating the solution with a standard acid solution. But this procedure usually requires that the solution should be heated to the boiling temperature. At the ordinary temperatures the acid reacts with the sodium carbonate to some extent to form the bicarbonate, thus:

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[1] Ztschr. phys. Chem., **12**, 167 (1893).

$$Na_2CO_3 + HCl = NaCl + NaHCO_3,$$

and this formation of the bicarbonate may possibly be augmented by some of the liberated carbonic acid acting on the still undecomposed carbonate. Acid sodium carbonate is itself neutral towards indicators, and in consequence totally misleading results are inevitable. Furthermore, the presence of bicarbonates in the solution, other than that formed by the hydrolytic action of the water, will render an estimation of the sodium alone utterly valueless. The problem has been presented in this laboratory to estimate the amount of sodium carbonate in mixtures containing also the bicarbonate and, further, to do this without heating the material. Many attempts have been made by others to devise a method for this purpose. That proposed by Winkler has probably proved the most satisfactory. A good description of it has been given by Küster.[1] But this method was not adapted to our purposes for several reasons. The method of Sundstrom, described by Lunge,[2] as well as that devised by Lunge[3] himself, were also found to be impracticable under the conditions which confronted us. Without going into greater detail it may be said that no method of which a description could be found in the literature was free from serious objections. This appeared most surprising in view of the probable technical value of such a method in the manufacture of sodium carbonate. The problem has been satisfactorily solved and an account of the preliminary work on it may be found elsewhere.[4] It was deemed advisable, however, to give the method a more critical examination. The results are recorded in this paper.

Acid potassium sulphate is a well-characterized strong acid.

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[1] Ztschr. anorg. Chem., **13**, 127 (1896).

[2] Ztschr. angew. Chem., 41 (1897).

[3] *Ibid.*, 169 (1897).

[4] Report No. 64; U. S. Department of Agriculture, Division of Soils.

With sodium carbonate it has been shown to react as here indicated:

$$Na_2CO_3 + HKSO_4 = HNaCO_3 + NaKSO_4.$$

The reaction-products, sodium bicarbonate and sodium potassium sulphate, are neutral towards the ordinary indicators. Therefore, by titrating a solution containing sodium carbonate with a standard solution of sodium or potassium bisulphate, the amount of sodium carbonate present can be determined directly. Obviously the same statements may be made regarding potassium carbonate. Many indicators have been used with this method, but it may be said at once that, while good results can be obtained with others, phenolphthalein lends itself preeminently to the purposes here in view, and it alone is now used in this work in this laboratory. It is to be regretted that the reverse procedure from that just stated cannot be followed, for to the majority of analysts it would certainly be easier to titrate to the appearance of color rather than to its disappearance. But in this case such a procedure is entirely inadmissible because the sodium carbonate, on being brought in contact with an excess of the strong acid, is more or less decomposed, with the evolution of carbon dioxide, and misleading results that are not comparable are obtained.

It has become evident, in the course of the investigation, that acid sodium carbonate is a very unstable salt, especially in water solutions. The sodium carbonate solutions which had been titrated to loss of color, immediately began to color again on standing, the rate of this "inversion" being a function of the concentration and the temperature, as well as time. Some solutions which had been titrated just to loss of color at 1° C. had practically no color at the end of an hour, but on being gradually warmed over a Bunsen flame very soon became strongly colored from the reaction of the regenerated sodium carbonate on the phenolphthalein present. A tenth-normal solution, titrated just to loss of color, at the room temperature (about 25° C.) will show a marked pink color within five minutes and a strong color within half an hour.

A solution of sodium carbonate was divided into a number of portions in small Erlenmeyer flasks, and colored by the addition of phenolphthalein or litmus. Carbon dioxide was passed in until the solutions no longer showed any alkaline reaction with the indicators. They were then allowed to stand for several days. Some of the flasks were closed with rubber stoppers. The open flasks very soon showed a strong alkaline reaction. In the closed flasks, while a faint alkaline color appeared within a very short time, the color became more intense, but very slowly, showing the influence of the carbon dioxide in retarding the inversion. Nevertheless, it would appear that the inversion does take place, even though some carbonic acid must be present. This phase of the subject is now being studied in this laboratory, and the investigation will be continued as time and opportunity may permit.

In a qualitative sense precisely similar results were obtained with potassium carbonate and with sodium silicate, of which both yield acid salts which are unstable in water and at once invert to a greater or less extent. Sodium borate and disodium phosphate, being salts of weak acids, give an alkaline reaction in water solutions and can be very conveniently titrated to neutrality with acid potassium sulphate, but in neither case was any subsequent inversion observed.

Description of Experiments.

After some preliminary work it was deemed advisable to test the method by referring all solutions to a standard alkali solution, rather than by making the numerous gravimetric determinations which would otherwise be required. All the titrations were made from two burettes which previous experience had shown to be quite reliable. It was not thought necessary to calibrate them. The burettes were graduated to tenths (0.1 cc.) and smaller readings could be estimated. It was thought preferable, however, not to attempt readings closer than one-half a scale division (0.05 cc.) but to depend upon the average of a series of readings.

The standard for reference was a solution of potassium hydrate, accurately prepared and carefully freed from carbonates or other impurities. It was so prepared as to contain 18.17106 grams of potassium hydroxide per liter. A solution of approximately tenth-normal acid potassium sulphate was then made up and compared with the standard potassium hydrate solution. It was found, as a result of a satisfactory series of titrations, that 1 cc. of the potassium hydrate solution was equivalent to 6.764 cc. of the acid potassium sulphate solution. It follows that 1 cc. of the acid potassium sulphate solution contained 0.006518 gram of the acid salt, whereas a tenth-normal solution (N/10) would contain 0.006758 gram.

Reasonably pure potassium bisulphate is not difficult to obtain. But one cannot always be certain that an otherwise satisfactory sample contains precisely those proportions of the elements involved, which are required by the formula $HKSO_4$. A small excess of either sulphuric acid or the potassium sulphate will not materially alter the value of the reagent for the purposes under discussion, but it is obvious that for very accurate work it is safer to determine the concentration of the solution in the manner just described, rather than depend on either a gravimetric determination of the sulphuric acid alone or of the potassium it contains.

A solution of potassium carbonate (approximately tenth-normal) was then prepared and titrated with the results here given, the first column indicating quantity of potassium carbonate, the second column the quantity of potassium bisulphate, and the third column the ratio of the readings:

Table I.

10.00	12.70	1.270
15.00	18.90	1.260
15.00	18.90	1.260
20.00	25.20	1.260
20.00	25.20	1.260
		1.262

These titrations were made in the usual manner by adding a little of the acid solution, shaking, and waiting a few moments to see if color disappeared before proceeding.

The potassium carbonate was then analyzed in the following way: The solution was treated with an excess of hydrochloric acid, boiled to drive off all the carbon dioxide liberated, and the excess of acid determined by titration with the standard potassium hydrate solution. The figures follow. The first column represents amounts of potassium carbonate, the second column hydrochloric acid, and the third column potassium hydrate:

Table II.

40.00	20.00	7.15
40.00	20.00	7.15
40.00	20.00	7.20
		7.166

By a careful and satisfactory series of titrations 1 cc. of the hydrochloric acid solution was shown to be equivalent to 1.0464 cc. of the potassium hydroxide solution. Therefore:

20 cc. HCl solution = 20.928 cc. KOH solution.
Excess " " = 7.166 " " "

40 cc. Na_2CO_3 " = 13.762 " " "
1 " " " = 0.344 " " "

It has been shown that 1 cc. KOH solution was equivalent to 6.764 cc. $HKSO_4$ solution; therefore, 0.344 cc. KOH solution was equivalent to 2.327 cc. $HKSO_4$ solution. But since only one-half as much acid potassium sulphate is required to convert the potassium carbonate to bicarbonate it should have required 2.327 ÷ 2, or 1.163 cc., instead of 1.262 cc. as actually found. This disagreement was startling in view of the good results previously obtained with the method.

A sodium carbonate solution of about the same strength as the potassium carbonate solution just described was prepared and a long series of titrations made in the same manner as with the potassium carbonate solution. It was found that 1 cc. of the carbonate solution was equivalent to 1.137 cc. of the acid sulphate solution, though an analysis made in the same manner as in the case of the potassium carbonate showed that 1.035 cc. of the acid sulphate solution should have been required. The disagreement was practically the same in both cases.

Two series of titrations were then made with the potassium carbonate solution. In the first series the potassium carbonate solution was heated to boiling in each case before titrating. In the second series in each case the solution was filled with crushed ice and shaken until the temperature was lowered to less than 1° C. before titrating. The number of cubic centimeters of the acid sulphate solution required to neutralize 1 cc. of the potassium carbonate solution was:

	cc.
At 0°–1° C.	1.455
" room temperature (about 26° C.)	1.262
After boiling (about 97° C.)	1.210

From these results it would appear that the reaction was more complete at the higher temperature, in spite of the fact that the inversion of the acid potassium carbonate is more rapid at these higher temperatures and might be expected to produce exactly opposite results. For instance, the solutions which had been titrated at 97° were very strongly colored within five minutes after the titration was completed, while those which were titrated at 1° showed only a faint pink color after standing for upwards of an hour. The true explanation of the results, however, became apparent in the course of these titrations. It was found that it takes a measurable time for the reaction between the acid sulphate and carbonate to run to end, and that if the acid sulphate is delivered too rapidly from the burette a considerable excess may be run into the carbonate solution before the color of the indicator disappears so that, with these two effects of inversion of the acid carbonate and the relatively slow reaction velocity between the carbonate and acid working against each other, it would be possible to run in the solution at such a rate as to obtain any desired result within quite wide limits, and, in fact, beautifully comparable results were thus obtained. The value of the method would be very slight if the personal equation could not be eliminated in the titrations. That this can be done, however, was clearly demonstrated. If the acid potassium sulphate solution is delivered from the burette at about the rate of 2 drops per second, and the vessel containing the alkaline carbonate is *constantly* and *vigorously* shaken, markedly lower reading will be obtained than by any other procedure; furthermore, the readings thus obtained were found to be quite independent of the temperature at which the titrations were made. These facts were confirmed by several long and satisfactory series of titrations. This point having been clearly established, a solution of sodium carbonate was carefully prepared and boiled for some time to complete the inversion of any acid sodium carbonate which might be present. After being cooled to room temperature and made up to the desired volume, it was titrated with the following results: The first column represents the amount of carbonate, the second column the amount of acid sulphate, and the third column the ratio of the readings.

Table III.

20.00	21.50	1.075
20.00	21.60	1.080
30.00	32.30	1.076
30.00	32.30	1.076
		1.077

The sodium carbonate solution was then analyzed by boiling with an excess of acid potassium sulphate and titrating the excess of acid with a solution of potassium hydrate of known concentration. The results are here given; the first column indicating amounts of carbonate taken, the second column amounts of acid potassium sulphate, and the third amounts of potassium hydrate required to neutralize the excess of acid:

Table IV.

20.00	50.00	5.50
20.00	50.00	5.50
20.00	50.00	5.50
20.00	50.00	5.50
		5.50

1.00 cc. KOH solution = 1.352 cc. $HKSO_4$ solution.
5.50 " " " = 7.436 " " "
20.00 " Na_2CO_3 " = 43.564 " " "
1.00 " " " = 2.128 " " "

But since only one-half as much acid potassium sulphate would be required to convert the carbonate to acid carbonate, 1 cc. of the Na_2CO_3 was equivalent to 2.128 cc. ÷ 2 or 1.064

cc. of the $HKSO_4$ solution. Comparing the value found by direct titration, 1.077 cc., the error for 1 cc. was about 1.2 per cent. More accurate results have, however, been obtained for both sodium carbonate and potassium carbonate. This error would amount to 0.10 cc. in reading for 10 cc., about 0.25 cc. for 20 cc., or nearly 0.50 cc. in reading a titration of 30 cc. But it has been shown repeatedly that readings for this amount could be obtained by different observers agreeing to within less than 0.20 cc., and it may be said that the probable error for such an amount is certainly no greater than this. Considering the number and nature of the operations involved, the agreement obtained above was considered satisfactory, and it was not deemed worth while to repeat the work merely for the purpose of being able to present more refined figures.

In order to demonstrate that the presence of sodium bicarbonate in the salt analyzed does not affect the accuracy of the method, mixtures of the carbonate and bicarbonate were prepared. Before titrating these mixtures with the acid potassium sulphate solution, the solutions of the carbonate and bicarbonate were separately titrated with this reagent. In Table V the first column represents amounts of sodium carbonate taken, the second column the amounts of acid potassium sulphate required to neutralize them respectively, and the third column the ratio of the readings :

Table V.

10.00	8.90	0.890
20.00	17.50	0.875
30.00	26.30	0.876
15.00	13.29	0.886
10.00	8.90	0.890
20.00	17.60	0.880
20.00	17.60	0.880
30.00	26.45	0.882
30.00	26.45	0.882
30.00	26.45	0.882
		0.882

A solution of sodium bicarbonate was then prepared and allowed to stand until equilibrium had been reached with the inverted normal carbonate. It was then titrated with the results here given:

Table VI.

25.00	14.60	0.586
10.00	5.90	0.590
10.00	6.10	0.610
10.00	6.10	0.610
20.00	12.30	0.615
		0.602

Mixtures were then made by adding 10 cc. of the sodium bicarbonate solution to 20 cc. of the normal sodium carbonate solution and titrating as before. The first column represents the amount of acid potassium sulphate solution required, the second column gives the reading corrected for the sodium bicarbonate added, and the third column the corresponding amount of acid required to neutralize 1 cc. of the sodium carbonate solution taken:

Table VII.

23.70	17.68	0.884
23.75	17.73	0.886
23.70	17.68	0.884
		0.885

The agreement of this figure 0.885 with that found in Table V, 0.882, is very satisfactory, and may be regarded as establishing the point under investigation. It should be remembered, however, that when sodium carbonate is added to a solution containing sodium bicarbonate and consequently some inverted carbonate, the equilibrium between the two substances may well be materially altered. In solutions as dilute as those examined, this displacement was probably very small and so did not interfere with the demonstration of the fact that the presence of acid sodium carbonate does not interfere with the estimation of the hydrolyzed sodium in the solution. But when the concentrations are considerable, this equilibrium displacement may well become an important factor. Should this method ever commend itself to use in technical work, this displacement of the equilibrium corresponding to an apparent increase of the amount of normal carbonate present on dissolving mixtures must be considered.

An interesting extension of the method has been developed in the course of our work. It is frequently necessary to make a rapid determination of the chloride as well as the carbonates in solution. This may be done in the following way: As soon as the solution containing the carbonate has been titrated to neutral action with acid potassium sulphate, a drop or two of this reagent is added in excess to retard the inversion of the bicarbonate to the normal alkaline carbonate. A small amount of a solution of potassium or ammonium chromate is then added as an indicator, and the solution titrated at once with a standard solution of silver nitrate. Before titrating with the silver nitrate the solution may be boiled, in which case the inverted carbonate must again be neutralized before making the determination for the chloride. But little advantage is gained thereby, however, and results in every way satisfactory have been repeatedly obtained, working throughout at the room temperature. For instance, a solution (tenth-normal) of sodium carbonate was prepared by standardizing against a tenth-normal (N/10) solution of acid potassium sulphate; also a solution of sodium chloride, 1 cc. of which was equivalent to 1.734 cc. of a tenth-normal solution of silver nitrate. The following are the results obtained with the mixtures of the sodium carbonate and sodium chloride solutions: The first column represents amounts of sodium carbonate taken, the second column the amounts of sodium chloride taken, the third column the amounts of acid potassium sulphate required to neutralize the mixtures, and the fourth column the amounts of silver nitrate required to precipitate the chloride present.

Table VIII.

5.00	10.00	5.05	17.35
10.00	10.00	10.10	17.35
15.00	10.00	15.20	17.35

The agreement shown in these results leaves nothing to be desired, and many more equally satisfactory determinations have been made. An interesting theoretical point is involved in the operation just described. The presence of normal carbonates in the solution would, it is well known, interfere with a titration for chloride with silver nitrate, as insoluble silver carbonate would be formed to some extent and interfere with the desired precipitation of the chloride. The reaction is to be regarded as the result of the silver ions $\overset{+}{\mathrm{Ag}}{}'$ coming in contact with the carbonic acid ions $\overset{-}{\mathrm{CO}}{}_3'$. But no such reaction is to be observed in the case we have been discussing, where acid sodium carbonate is in the solution. Therefore it appears reasonable to assume that acid sodium carbonate does not yield a $\overset{-}{\mathrm{CO}}{}_3$ ion, but probably dissociates, thus

$$\mathrm{NaHCO_3} \rightleftarrows \overset{+}{\mathrm{Na}} + \mathrm{H}\overset{-}{\mathrm{CO}}{}_3$$

and the ion $\mathrm{H}\overset{-}{\mathrm{CO}}{}_3$ does not react with the silver ion to give an insoluble compound. There is further evidence to support this view.[1]

If a solution of acid sodium carbonate is added to a solution of a barium salt there is only a little precipitate formed at first, though the precipitation of the barium generally proceeds and is completed in time, more quickly if the solution be heated. It has been shown that acid sodium carbonate in water solution is unstable, some normal carbonate being formed at once, and it is to this small amount of normal carbonate that the first precipitation of the barium is due. But when this has taken place the equilibrium between the sodium carbonate and acid sodium carbonate is destroyed, more sodium carbonate is formed, and the precipitation of the barium again proceeds. This action is, of course, continuous. As the inversion of the acid sodium carbonate is more rapid at high temperatures, the formation of the normal carbonate and subsequent precipitation of the barium will proceed more rapidly on heating.

The use of ammonium carbonate in precipitating insoluble carbonates seems worthy of consideration in this connection. Unlike the corresponding sodium and potassium salts, ammonium carbonate is unstable in water solution, breaking down with the formation of the acid carbonate and the escape of some of the ammonia as such. But an equilibrium is established between the normal carbonate and the acid carbonate, which is destroyed when the solution is brought into contact with some salt which will precipitate an insoluble carbonate, such as calcium or barium. The inversion of the acid carbonate is measurably slow, however, and, as is well known, to obtain complete precipitation the solution must be allowed to stand for some time or be heated.

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[1] Walker and Cormack: J. Chem. Soc., **47**, 5 (1900); Foundations of Analytical Chemistry; Ostwald and McGowan, pp. 193 and 207.

A statement of some of the preliminary experiments on the inversion phenomena referred to may be of interest in this connection. Three portions of a sodium carbonate solution were titrated with acid potassium sulphate to loss of color with phenolphthalein as indicator, allowed to stand for twenty-four hours, and then titrated a second time to loss of color. The results are here given, the first column being amounts of the carbonate solution, the second column amounts of acid sulphate added, and the third column amounts of acid sulphate required to neutralize the solution after standing.

Table IX.

10.00	8.90	1.00
20.00	17.50	1.85
30.00	26.30	2.55

It would appear that the inversion was approximately proportional to the initial amount of the bicarbonate, but as the concentrations were not quite the same and the sulphates present may have an influence, this conclusion can only be drawn tentatively. Some measurements, which have been made by Mr. Lyman J. Briggs, indicate that the inversion at first approaches a maximum quite rapidly, but, when equilibrium has been nearly reached, it becomes very slow and probably requires a long time before reaching final equilibrium.

Three portions of 20 cc. of a potassium carbonate solution were each titrated to disappearance of alkaline reaction with 24.2 cc. of the acid potassium sulphate solution and, after standing forty-eight hours, each required 3.1 cc. of the acid sulphate solution to neutralize them.

Ten cc. of a sodium silicate solution required 14.1 cc. of the acid sulphate solution to neutralize it. It was immediately boiled for three minutes, after which it required 1.1 cc. of the acid sulphate solution to neutralize it; another portion of 10 cc., to which 14.1 cc. of the acid sulphate had been added after the expiration of an hour, at the room temperature, required 0.9 cc. to neutralize it. The case of the sodium bisilicate differs essentially, however, from that of the sodium bicarbonate, in that no volatile component can be formed. So that this *apparent* inversion must be more limited in amount and is in reality a measure of the hydrolysis of the salt. It was not appreciable in the case of the borates or phosphates, as has already been noted.

An application of the method to a solution of sodium silicate was made. Table X gives the results of the titrations of the solution with the acid potassium sulphate, the first column indicating amounts of the silicate solution, the second column amounts of the acid sulphate, and the third column the corresponding ratios:

Table X.

20.00	31.00	1.550
20.00	31.00	1.550
10.00	15.70	1.570
10.00	15.80	1.580
10.00	15.50	1.550
10.00	15.70	1.570
15.00	23.60	1.573
15.00	23.60	1.573
20.00	31.40	1.570
20.00	31.45	1.572
		1.566

The solution was then analyzed by adding an excess of hydrochloric acid, boiling, and titrating the excess of the acid with a solution of potassium hydroxide. The first column of Table XI indicates the amounts of silicates taken, the second column the amounts of hydrochloric acid added, and the third column the amounts of potassium hydrate required to neutralize the excess of acid:

Table XI.

40.00	20.00	11.70
40.00	20.00	11.70
40.00	20.00	11.70
		11.70

Since in this case the silicic acid does not escape from the solution as does carbonic acid, when the hydrochloric acid is added to excess, enough potassium hydrate will be required not only to neutralize the excess of hydrochloric acid, but also to reconvert the silicic acid to potassium bisilicate before the solution will be alkaline.

20.00 cc. HCl solution = 20.928 cc. KOH solution.
Excess of " " = 11.700 " " "
40.00 cc. sodium silicate solution = 9.228 " " "
1.00 cc. sodium silicate solution = 0.231 " " "

It has been shown that 1 cc. KOH solution was equivalent to 6.764 cc. $HKSO_4$ solution, therefore 0.231 cc. KOH solution was equivalent to 1.562 cc. $HKSO_4$ solution. The agreement of this figure 1.562 cc. with that given in Table X, 1.566 cc., must be regarded as entirely satisfactory.

Summary.

The principal results of this investigation may be summarized as follows:

1. The amount of a soluble alkaline carbonate in a solution can be quickly and accurately determined whether the bicarbonates are present or not.
2. The method seems well adapted to the estimation of silicates, borates, phosphates, and the salts of weak acids in general.
3. The bicarbonates are unstable in water solution and are more or less completely converted into the normal salt.
4. Alkaline bicarbonates are themselves neutral in water solutions; they do not yield a CO_3 ion by hydrolysis, or they do so only to a slight extent.

5. Therefore, an accurate volumetric determination of chlorides by means of a standard silver nitrate solution is feasible in the presence of alkaline bicarbonates, if the hydrolysis of these latter is prevented.

Contributions from the Chemical Laboratories of the Massachusetts Institute of Technology.

XXV.—ON THE ISOMORPHISM OF SELENIUM AND TELLURIUM.

BY JAMES F. NORRIS AND RICHARD MOMMERS.

The fact that the most trustworthy determinations of the atomic weight of tellurium have given results which place it in the eighth group in the periodic system of the elements, has led to a study of the analogies existing between tellurium and the platinum metals on the one hand, and sulphur and selenium on the other. Retgers,[1] in his work on isomorphism, studied carefully the relations between sulphur, selenium, and tellurium, and concluded that while sulphur and selenium showed complete crystallographic similarity in their compounds, tellurium was not isomorphous with either element. The only occurrence of isomorphism between tellurium and the elements of the oxygen family was in the case of the sulphides, selenides, and tellurides. These compounds crystallize in the cubic system and, consequently, according to Retgers, possess such a high state of crystallographic symmetry that their power to form mixed crystals should not be taken as a proof of the true isomorphism of their constituents. Potassium tellurate is not isomorphous with potassium selenate, but is isomorphous with potassium osmate.

Muthmann[2] showed later that the double bromide of potassium and tellurium is isomorphous with the corresponding salt containing selenium. Retgers[3] pointed out in reply, that the tellurium compound is also isomorphous with the analogous platinum salt and that, as is the case with the selenides and tellurides, the formation of mixed crystals is due to the fact that all of the compounds crystallize in the cubic system.

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[1] Ztschr. phys. Chem., **8**, 70; **10**, 533.

[2] Ber. d. chem. Ges., **26**, 1011.

[3] Ztschr. anorg. Chem., **12**, 105.

As no case of true isomorphism between selenium and tellurium compounds has been proved, it seemed of interest to question further. The crystallography of the double bromide of platinum and dimethylamine has been studied carefully by Hjortdahl.[1] The salt crystallizes in the orthorhombic system, has the faces $\infty\breve{P}2$ and $\breve{P}\infty$, and the axial ratio 0.9903 : 1 : 0.9927. As the argument brought forward against the value of conclusions drawn from the formation of mixed crystals in the cubic system could not hold in this case, we compared this salt with the analogous selenium and tellurium compounds. The double bromide of selenium and dimethylamine had been prepared by one of us,[2] but its crystallography had not been studied. As the tellurium compound had not been made, it was prepared and was found on analysis to resemble in composition the other two salts.

The compound containing selenium crystallizes in stout, prismatic needles, terminated by domes, which closely resemble the platinum double bromide. The crystals of the tellurium salt are like those of the other two salts, with the exception that well-developed macropinacoids are present at times. The color of the compound, however, is different from that of the selenium and platinum salts; the latter are nearly alike, having a dark-red color resembling that of chromic acid, while the color of the tellurium salt is almost that of azobenzene.

As the facilities were not at hand for a complete crystallographic investigation, the isomorphism of the salts was studied by applying the test of the formation of mixed crystals in the manner devised by Retgers.[3] In using this method saturated solutions of two salts, which must differ in color, are placed side by side on a microscope slide and then are brought together with a glass rod. The crystals formed on evaporation are examined under a microscope. If the salts are isomorphous, the color of the crystals varies gradually from one side to the other, the crystals of the pure compounds being visible on the extreme edges of the mass. If, however, the salts are not isomorphous, they do not mix, and in the center where the two solutions have been brought together, distinct crystals of each compound can be seen owing to their difference in color. In studying the isomorphism of two colored salts, Retgers made use of a third salt, which was colorless. If both of the colored salts formed mixed crystals with the colorless salt, the former were considered isomorphous with one another.

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[1] Jsb. d. Chem., 1882, 474.

[2] This JOURNAL, 20, 490.

[3] Ztschr. phys. Chem., 8, 6.

As the double salts which were to be investigated were somewhat alike in color, their isomorphism could be determined only by comparing each salt separately with a fourth salt having a different color. The double chloride of tellurium and dimethylamine was found to answer the purpose admirably. The compound crystallizes in light-yellow prisms, which have the same forms as the analogous bromide. The chloride formed mixed crystals of varying depths of color with the selenium and tellurium double bromides, but did not mix with the platinum compound. In the latter case the platinum salt crystallized in small, well-defined, dark-red crystals, which were at times overgrown with the tellurium salt. Solutions of the selenium, tellurium, and platinum bromides were mixed separately with a solution of the chloride and allowed to crystallize. The crystals obtained in the first two cases were uniform in color, whereas with the platinum salt two kinds of crystals were distinctly seen. It appears, then, that the double bromides containing selenium and tellurium are both isomorphous with the chloride, and are, therefore, isomorphous with one another. The platinum compound, however, does not form mixed crystals with the chloride and is not isomorphous with the analogous selenium and tellurium salts. The work has established the first case of isomorphism between selenium and tellurium compounds which is not open to the objections raised by Retgers.

The existence of isomorphism in the case of the double bromides appears to be inconsistent with the fact that potassium tellurate is not isomorphous with potassium selenate. The lack of crystallographic similarity in this case is not remarkable, inasmuch as one salt contains water of crystallization while the other is anhydrous. In order to get further evidence for or against the isomorphism of the two elements in their oxygen acids, the cesium, rubidium, and cerium salts of selenic and telluric acids are being prepared and studied.

In an investigation by one of us of the double chlorides and bromides of selenium and dimethyl- and trimethylamine a number of salts were obtained which possessed very unusual compositions for compounds of this class. With dimethylamine, compounds of the following formulæ were prepared :

$2SeOCl_2.3(CH_3)_2NH.HCl$,
$SeO_2.(CH_3)_2NH.HCl$,
$2SeBr_4.SeBr.3(CH_3)_2NH.HBr$,
$SeBr_4.2(CH_3)_2NH.HBr$,
$SeBr_4.2[(CH_3)_2NH.HBr_2]$,
$SeBr_4.2[(CH_3)_2NH.HBr_2].(CH_3)_2NH.HBr$.

In order to discover if tellurium resembled selenium in the power to form such oxysalts and perhalides, we undertook the preparation of all the possible double chlorides and bromides of tellurium and dimethylamine. The uncertainty about the relation of tellurium to the periodic law noted above, adds interest to any new facts brought to light and to any new analogies established. As a result of the work, compounds having the following formulæ were prepared :

$3TeCl_4.TeOCl_2.4(CH_3)_2NH.HCl.H_2O$,
$TeCl_4.TeOCl_2.2(CH_3)_2NH.HCl.H_2O$,
$TeCl_4.2TeOCl_2.3(CH_3)_2NH.HCl$,
$TeCl_4.2(CH_3)_2NH.HCl$,
$TeBr_4.2(CH_3)_2NH.HBr$.

A consideration of the above formulæ shows that tellurium, as well as selenium, forms double salts which contain the oxychloride of the metal. With the more basic tellurium, however, the tetrachloride enters into the compound. The first three salts in the list were obtained from solutions containing a large excess of tellurium. These salts, which at first appear to have very complicated formulæ, can be considered as derivatives of the salt $TeCl_4.(CH_3)_2NH.HCl$, in which a part of the tellurium tetrachloride has been converted into the oxychloride by the water present in the solvent from which the salts were crystallized. They all contain the tellurium and the amine in the molecular ratio of 1 : 1. In the first salt $\frac{1}{4}$ of the tetrachloride has been changed into oxychloride, in the second $\frac{1}{2}$, and in the third $\frac{2}{3}$. The formation of the various salts was determined by the amount of hydrochloric acid present during crystallization.

Double salts containing selenium and the perbromide of dimethylamine, $(CH_3)_2NH.HBr_3$, were readily prepared. The salts crystallized well from hydrobromic acid and dissolved in water with the evolution of bromine. With tellurium bromide analogous salts could not be formed. An unsuccessful attempt was made to prepare double salts containing the amine perbromide and platinum and lead. As far as our experiments go, selenium is the only element which forms salts of this class.

Wheeler[1] prepared two double bromides of tellurium and potassium, one of which contained water of crystallization. The double bromide of dimethylamine and tellurium was prepared under conditions favorable to the formation of a hydrated salt, but the resulting compound contained no water of crystallization.

The analogies in composition exhibited by the selenium and tellurium salts are as great as could be expected; the differences observed are well explained by the more metallic nature of tellurium.

Experimental.

The double salts were prepared by dissolving tellurium dioxide and dimethylamine hydrochloride or hydrobromide in the corresponding halogen acid and evaporating the solutions to crystallization. Seven different mixtures were prepared in each case in which the proportions of the constituents varied from 4 molecules of the oxide to 1 of the amine salt to 1 of the oxide to 4 of the salt.

In the analyses, tellurium, halogen, and the amine were determined. An attempt was made to estimate the water of crystallization in the hydrated chlorides, but without success, for even at 80°–90° the salts could not be brought to a constant weight owing to the volatilization of a part of the tellurium tetrachloride. The presence of water was shown, however, qualitatively. The tellurium was determined volumetrically by the method of Norris and Fay[1] after the amine had been removed by heating with a solution of sodium hydroxide. In some of the compounds the halogen was estimated gravimetrically; in the analysis of the others the volumetric method of Volhard was used. The method was shown to be accurate in the presence of tellurium by an analysis of the double bromide of tellurium and potassium.

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[1] Am. J. Sci. [3], **45**, 267.

Salt of the Composition $TeCl_4.2(CH_3)_2NH.HCl$.—This compound is obtained readily by evaporating to crystallization a mixture of tellurium dioxide and dimethylamine hydrochloride, in the theoretical proportions, dissolved in dilute hydrochloric acid. The salt crystallizes in light-yellow, stout, lustrous needles from a hot solution. When obtained by spontaneous evaporation the crystals are well-developed prisms, which are probably orthorhombic, modified by brachydomes and macropinacoids. The salt is soluble in a small amount of water. Excess of the solvent causes decomposition into tellurous acid, which separates as a curdy, white precipitate. It dissolves readily in alcohol and is insoluble in ether. The results of the analyses follow:

I. 0.2634 gram salt gave 0.1293 gram Cl by the volumetric method.
0.3396 gram salt gave 0.0986 gram Te.
II. 0.2508 gram salt gave 0.1237 gram Cl.
0.3053 gram salt gave 0.0897 gram Te.
III. 0.3910 gram salt gave 0.0813 gram $(CH_3)_2NH$.

	Calculated for $TeCl_4.2(CH_3)_2NH.HCl$.	Found. I.	II.	III.
Cl	49.20	49.10	49.35	....
Te	29.43	29.41	29.38	....
$(CH_3)_2NH$	20.84	....	....	20.79

Salt of the Composition $TeCl_4.TeOCl_2.2(CH_3)_2NH.HCl.H_2O$.—When a solution containing tellurium dioxide and dimethylamine hydrochloride, in the molecular ratio of three of the former to one of the latter, dissolved in dilute hydrochloric acid (sp. gr. 1.12), is allowed to evaporate slowly two well-crystallized compounds are formed. The salt of the above composition first separates in compact, almost colorless, crystals, which completely cover the bottom of the containing vessel. Stout, yellow needles are next formed. The two compounds can be separated mechanically without difficulty, as the yellow crystals are from 0.5–1 centimeter in length. The compound closely resembles in composition the bromide of selenium and trimethylamine, which has the formula $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$. An analysis gave the following results:

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[1] This JOURNAL, **20**, 278.

I. 0.2624 gram salt gave 0.4535 gram AgCl.
II. 0.3275 gram salt gave 0.1251 gram Te.
III. 0.3055 gram salt gave 0.0425 gram $(CH_3)_2NH$.

	Calculated for $TeCl_4.TeOCl_2.2(CH_3)_2NH.HCl.H_2O$.	Found. I.	II.	III.
Cl	42.74	42.79	....	....
Te	38.32	....	38.20	....
$(CH_3)_2NH$	13.58	....	....	13.90

Salt of the Composition $3TeCl_4.TeOCl_2.4(CH_3)_2NH.HCl.H_2O$.—This salt was always formed under the conditions made use of in the preparation of the compound described above. The crystals were so well developed and large that they could be obtained pure for analysis without difficulty. The salt forms stout, columnar, rectangular, yellow crystals, whose ends are truncated by a single plane at a sharp angle to the prismatic faces. It was not very stable in the air, readily losing its bright luster, and consequently its crystallography was not carefully studied. The analytical results follow:

I. 0.3056 gram salt gave 0.5767 gram AgCl.
0.3691 gram salt gave 0.1375 gram Te.
II. 0.2675 gram salt gave 0.5056 gram AgCl.
0.3151 gram salt gave 0.1169 gram Te.
III. 0.3334 gram salt gave 0.0447 gram $(CH_3)_2NH$.

	Calculated for $3TeCl_4.TeOCl_2.4(CH_3)_2NH\ HCl.H_2O$.	Found. I.	II.	III.
Cl	46.77	46.71	46.79	....
Te	37.27	37.26	37.11	....
$(CH_3)_2NH$	13.20	....	....	13.41

Salt of the Composition $TeCl_4.2TeOCl_2.3(CH_3)_2NH.HCl$.—As two salts were obtained which were derivatives of the compound $TeCl_4.(CH_3)_2NH.HCl$, in which different proportions of the tetrachloride were converted into the oxychloride, the effect of varying the concentration of the hydrochloric acid from which the salts were crystallized, was investigated.

Tellurium dioxide and dimethylamine hydrochloride in the molecular ratio of three of the former to one of the latter were dissolved in the smallest quantity of concentrated hydrochloric acid possible. After standing two months in a desiccator the solution became very viscous and crystals separated slowly. These were removed, but it was found impossible to purify them for analysis. The crystals did not resemble any of the other chlorides which had been prepared and were probably a different compound.

To effect the greatest decomposition into the oxychloride, tellurium tetrachloride and the amine salt, in the proportions used in the experiment just described, were dissolved in water acidulated with just enough hydrochloric acid to keep the solution clear. After long standing a pale greenish-yellow salt separated in the form of stout prismatic crystals, truncated by domes. A careful study of the crystallography of the salt was impossible. It will be seen from the formula of the salt that complete decomposition of the tetrachloride did not take place.

The selenium compound prepared under the same conditions, however, contained no tetrachloride. The results of the analysis of the salt are as follows:

I. 0.2736 gram salt gave 0.4633 gram AgCl.
0.2987 gram salt gave 0.1213 gram Te.
II. 0.3096 gram salt gave 0.5227 gram AgCl.
0.3060 gram salt gave 0.1240 gram Te.

	Calculated for $TeCl_4.2TeOCl_2.3(CH_3)_2NH.HCl$.	Found.	
		I.	II.
Cl	41.41	41.94	41.79
Te	40.52	40.63	40.52

Salt of the Composition $TeBr_4.2(CH_3)_2NH.HBr$.—A salt of this composition was the only bromide obtained as the result of a large number of experiments. Mixtures similar to those used in the preparation of the chlorides were made. From these, crystals were obtained by slow evaporation in a desiccator, by rapid concentration by heat, and in the presence of bromine. The salt is prepared most readily by dissolving the theoretical quantities of tellurium dioxide and dimethylamine hydrobromide in dilute hydrobromic acid and evaporating to crystallization. The compound can be crystallized from water, although it is decomposed by a large excess of the solvent. The crystallography of the salt has been described in the first part of the paper. The analytical results follow:

I. 0.2246 gram salt gave 0.1546 gram Br.
0.5012 gram salt gave 0.0925 gram Te.
II. 0.2279 gram salt gave 0.1559 gram Br.
0.4659 gram salt gave 0.0846 gram Te.

	Calculated for $TeBr_4.2(CH_3)_2NH.HBr$.	Found. I.	 II.
Br	68.59	68.84	68.41
Te	18.24	18.46	18.15

BOSTON, March 9, 1900.

Contributions from the Chemical Laboratory of Harvard College.

CXVIII.—NOTE ON THE CONSTITUTION OF DIPARABROMBENZYLCYANAMIDE.[1]

BY C. LORING JACKSON AND R. W. FULLER.

The work described in this paper consists of the conversion of the silver salt of cyanamide into a dialkylcyanamide, and the determination of the constitution of this body. Last summer (after this work was finished) a paper appeared in the "Berichte der deutschen chemischen Gesellschaft," in which Wallach[2] described a number of substituted cyanamides obtained by the action of bromide of cyanogen on secondary amines. For fear of approaching too near the field thus reserved by Wallach we shall abandon the further study of dialkylcyanamides, but the study of alkyl compounds of dicyandiamide and dicyanimide will be taken up in this laboratory; in fact, work on this latter substance is already in progress.

Theoretically, a dialkylcyanamide derived from the silver salt of cyanamide might have either of the following formulas:

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[1] Presented to the American Academy of Arts and Sciences, December 13, 1899.
[2] Ber. d. chem. Ges., **32**, 1872.

R—N=C=N—R or R_2=N—CN, and it is easy to determine by experiment which of these two formulas is correct. So far as we can find, but a single experiment of this sort has been tried; this was published some years ago by Fileti and Robert Schiff,[1] who prepared diethylcyanamide by the action of ethyl iodide on argentic cyanamide at 100° for some hours. The product was extracted with ether, and divided into two portions; one was distilled, and gave a boiling-point of 186°, whereas Cloez and Cannizzaro,[2] who prepared it by the decomposition of ethylcyanamide, found a boiling-point of 190°. Fileti and R. Schiff analyzed their distillate, and obtained carbon 60.66 instead of 61.22, and hydrogen 10.11 instead of 10.30. The other portion of their product (which had not been distilled) was decomposed by means of hydrochloric acid on the water-bath; the chlorides obtained by evaporating the hydrochloric acid solution were converted into chlorplatinates and crystallized fractionally, when they obtained two end fractions in which the platinum was determined with the following results:

	Calculated for		Found.	
	$(NH_4)_2PtCl_6$.	$((C_2H_5)_2NH_2)_2PtCl_6$.	I.	II.
Pt	44.04[1]	35.30[1]	42.51	36.3

$(C_2H_5NH_3)_2PtCl_6$ requires 39.24[3] per cent of platinum.

In considering these results of Fileti and R. Schiff, it is to be observed that the diethylcyanamide was not purified, and that no very sharp criterion of purity was given (Wallach states that these substances are decomposed by distillation under ordinary pressure, so that the boiling-point is not of much value in this respect), further that their analyses of the platinum salts did not give numbers very near to those calculated. It seemed to us, therefore, worth while to try similar experiments with, if possible, a crystalline disubstituted cyanamide, which could, therefore, be obtained in a state of undoubted purity, and also with one which would yield amines more easily separated than ammonia and diethylamine. We selected for this purpose the diparabrombenzylcyanamide, since the parabrombenzyl compounds show a great tendency to crystallize, and the diparabrombenzylamine, if formed, could be recognized by its melting-point, 50° (dibenzylamine is a liquid), while the parabrombenzylamine, if that were the product, gives a carbonate with a definite melting-point, and both these amines could be separated without difficulty from ammonia.

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[1] Ber. d. chem. Ges., **10**, 425 (1877).

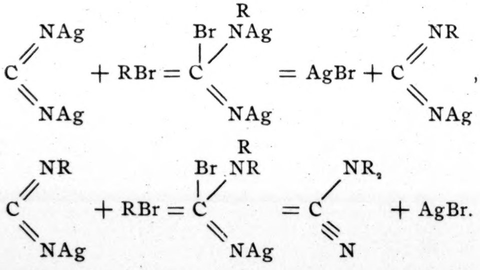
[2] Ann. Chem. (Liebig), **90**, 95.

[3] These are the numbers given by Fileti and R. Schiff. They would be somewhat altered by using modern atomic weights.

The diparabrombenzylcyanamide proved to be a well-crystallized solid, melting at 133°. On decomposition with dilute sulphuric acid it gave diparabrombenzylamine, ammonia, and carbonic dioxide by the following reaction :

$$(C_6H_4BrCH_2)_2NCN + 2H_2O = (C_6H_4BrCH_2)_2NH + NH_3 + CO_2.$$

Our results, therefore, confirm those of Fileti and R. Schiff, and leave no doubt that the dialkyl derivatives from argentic cyanamide are cyanamides and not carbodiimides. If they are formed by direct replacement of the silver in argentic cyanamide by the alkyl radicals, the same constitution (Ag_2NCN) must be ascribed to this substance and to cyanamide. If, on the other hand, these compounds are formed by successive additions of the alkyl bromide with splitting off of argentic bromide, the disubstituted cyanamides could be formed from a silver salt with a carbodiimide formula, as is shown by the following reactions :



Our results, therefore, prove nothing in regard to the true formula of cyanamide.

Preparation of Diparabrombenzylcyanamide, $(C_6H_4BrCH_2)_2NCN$.

The yellow silver salt of cyanamide, Ag_2NCN, prepared according to Walther,[1] was mixed with a benzol solution of parabrombenzyl bromide in the proportion of 2 molecules of bromide to 1 of the salt, which should be finely powdered. The mixture was heated in a flask with a return-condenser on the steam-bath, until after four or five hours the full yellow color of the argentic cyanamide had been completely replaced by the yellowish-white color of argentic bromide. The precipitate was then filtered out and washed thoroughly with hot benzol, and the filtrate and washings evaporated to dryness, when a thick reddish-yellow oil was left. To purify this it was dissolved in hot alcohol, and the strong solution allowed to cool slowly; a yellow oil was deposited, at first followed by a white crystalline substance, which was obtained by pouring the solution off from the oil as soon as the crystals began to appear. By repeated recrystallizations of this sort the melting-point of the substance was raised to 133°, where it remained constant. It was dried *in vacuo* and analyzed with the following results :

I. 0.1508 gram substance gave, by the method of Carius, 0.1494 gram argentic bromide.

II. 0.3041 gram substance gave 20.2 cc. nitrogen at 18°.6 and 760.4 mm. pressure.

	Calculated for $(C_7H_6Br)_2NCN$.	Found. I.	Found. II.
Br	42.11	42.18	....
N	7.37	....	7.64

In view of the great tendency of cyanamides to polymerize, it was thought safer to determine the molecular weight of the body[2] by the method of freezing a benzol solution, which gave the following results :

0.375 gram substance dissolved in 16.25 grams of benzol produced a depression of 0°.28 in the freezing-point.

	Calculated for $(C_7H_6Br)_2NCN$.	Found.
Mol. wt.	380	337

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[1] J. prakt. Chem., 1896, 510.

[2] This work was done before the appearance of Wallach's statement that disubstituted cyanamides show no tendency to polymerize.

There can be no doubt, therefore, that the substance is really $(C_6H_4BrCH_2)_2NCN$.

Properties of Diparabrombenzylcyanamide.

The substance crystallizes from benzol in sheaves of white crystals shaped like the blade of a lancet, sometimes united laterally into groups with comb ends. It melts at 133°. It is freely soluble in benzol, chloroform, acetone, or acetic ester; soluble in toluol; slightly soluble in cold ethyl or methyl alcohol or glacial acetic acid, freely soluble in these solvents when they are hot; slightly soluble in ether, carbonic disulphide, or in hot or cold water; essentially insoluble in ligroin. It is slowly decomposed by cold strong sulphuric acid; apparently unaffected by hydrochloric acid or nitric acid in the cold. The best solvent for it is hot alcohol.

In order to see if it could form a chloride, a portion of the diparabrombenzylcyanamide was dissolved in anhydrous benzol and saturated with dry hydrochloric acid gas. No precipitate was formed even after the mixture had stood for two weeks, and on evaporating off the benzol the original substance was recovered unaltered. It would seem from this experiment that the diparabrombenzylcyanamide cannot unite with hydrochloric acid.

A number of experiments were tried in the hope of obtaining polymers of the diparabrombenzylcyanamide. A dilute solution of sodic or potassic hydrate produced no effect on the substance, either by long standing in the cold or by boiling the mixture. The substance was boiled for two weeks with a solution of ammonic hydrate, care being taken to replace the ammonia which escaped, but the only change observed was that the color turned from white to pale-brown, evidently due to a slight decomposition, since the melting-point of the substituted cyanamide was essentially unaltered. Water alone was also tried at the boiling-point, but produced no change. Upon heating the substance above its melting-point it remained unaltered to 160°; above this point it turned first yellow, and at higher temperatures red, and on cooling gave an oily product, which we could not bring into a fit state for analysis. A similar viscous product was obtained when the substance was heated with sodic acetate. In both these cases it seemed evident that a decomposition had taken place rather than a polymerization, and our experiments, therefore, confirm the statement of Wallach that these dialkylcyanamides show no tendency to polymerize.

Decomposition of Diparabrombenzylcyanamide.

As some preliminary experiments showed that the substituted cyanamide was decomposed with difficulty by hydrochloric acid in open vessels, we adopted a dilute sulphuric acid having a specific gravity of 1.44, which has frequently given good results in this laboratory. Several grams of the diparabrombenzylcyanamide were boiled with a large excess of this acid in a flask with a return-condenser. Soon after the substance melted in the hot acid an effervescence was observed, and upon testing the gas given off with baryta water it proved to be carbonic dioxide. As the oily drops did not disappear, the heating was continued for ten hours, which reduced the amount of oil, but did not entirely remove it. On cooling, the whole liquid became filled with a voluminous white crystalline precipitate; we determined, therefore, to stop the process at this point and isolate this crystalline substance, which could be easily separated from the portion undissolved in the hot sulphuric acid. This latter substance, which solidified on cooling, seemed to consist of undecomposed diparabrombenzylcyanamide, as it gave a fresh quantity of the crystalline product on boiling again with sulphuric acid; its amount was insignificant. To obtain the crystalline product it was filtered from the acid liquid, washed with a little cold water to free it from adhering acid, and then dissolved in hot water, which left behind the few black lumps of undecomposed cyanamide. The solution was then filtered, and the sulphate decomposed by the addition of a strong solution of sodic hydrate, which set free the base as a pasty mass, solidifying on cooling. This base, after purification by crystallization from alcohol, showed the constant melting-point 50°, which is that of the diparabrombenzylamine,[1]

$$(C_6H_4BrCH_2)_2NH.$$

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[1] Jackson: This JOURNAL, 3, 251.

For greater security the chlorplatinate was prepared and analyzed. Chlorplatinic acid added to an alcoholic solution of the base gave a yellow precipitate, which was purified by washing with alcohol, and dried *in vacuo*.

0.1783 gram salt gave, on ignition, 0.0309 gram Pt.

	Calculated for $[(C_7H_6Br)_2NH_2]_2PtCl_6$.	Found.
Pt	17.58	17.34

The sulphuric acid filtrate from the crystals of the diparabrombenzylamine sulphate was treated at first with sodic carbonate, and finally with a large excess of sodic hydrate, and distilled with steam, the distillate being collected in a series of flasks containing hydrochloric acid. After the distillation was finished, the contents of the flasks were evaporated to dryness on the steam-bath, and the white residue dissolved in a little water and converted into the chlorplatinate; this was a yellow precipitate crystallizing in octahedra, which was washed with water and alcohol, dried *in vacuo*, and analyzed with the following results:

0.2061 gram chlorplatinate gave, on ignition, 0.0903 gram Pt.

	Calculated for $(NH_4)_2PtCl_6$.	Found.
Pt	43.91	43.81

It is evident from the experiment described above that the products of the decomposition of diparabrombenzylcyanamide, when boiled with dilute sulphuric acid, are carbonic dioxide, diparabrombenzylamine, and ammonia. The reaction, therefore, runs as follows:

$$(C_6H_4BrCH_2)_2NCN + 2H_2O = (C_6H_4BrCH_2)_2NH + NH_3 + CO_2.$$

ON THE EFFECT OF VERY LOW TEMPERATURES ON THE COLOR OF COMPOUNDS OF BROMINE AND IODINE.

By J. H. Kastle.

Some time ago the writer called attention to the fact that the characteristic red, orange, or yellow color of bromine and iodine compounds could probably be accounted for on the supposition that the halogen compounds exhibiting such colors are slightly dissociated even in the solid state; and that the characteristic color, therefore, is simply that of the halogen itself. The following facts were cited in support of this conclusion:

1. The color intensity of the halogens is in inverse ratio to their chemical activity, and may be represented roughly at least by $F < I$. Similarly, the color intensity of their compounds by $MF < MI$. Further, the color of bromine and iodine compounds is altogether similar to that exhibited by certain solutions of these two elements.

2. The perfect continuity exhibited in the color changes of such easily dissociable substances as phosphorus pentabromide in passing through the solid, liquid, and gaseous states.

3. Those halogen compounds are the most highly colored which are the least stable, and whose elements are held in combination by the weakest affinities.

4. On heating, the color of halogen compounds becomes darker and deeper in tint.

It also follows that, if the characteristic color of bromine and iodine compounds is due to dissociation, the color of these compounds ought to become lighter in tint, if not altogether white, on cooling to very low temperatures. At the time of my first communication on this subject, no opportunity was afforded for trying the effect of very low temperatures on the color of the compounds in question. Through the kindness of Dr. Freer, of the University of Michigan, and Dr. Simon, of the College of Physicians and Surgeons, Baltimore, I have recently been able to try the effect of very low temperatures (the boiling-point of liquid air -190°) on the color of certain of these halogen compounds. On the 9th of March, Dr. Freer lectured on liquid air in the city of Louisville, and on the 22nd of March Dr. Simon lectured in Cincinnati on the same subject. At the close of the lecture both of these gentlemen kindly placed at my disposal a quantity of the liquid. The following compounds were selected for experiment: Lead iodide, phosphorus pentabromide, phosphorus heptabromide, mercuric iodide,[1] iodoform, mercuric bromiodide, benzene dibromsulphonamide, and tribromphenol bromide. Small amounts of these compounds in pure condition were placed in sealed tubes. These were then immersed in liquid air in a Dewar tube and allowed to remain in the liquid until no further alteration of color was observable. The color of these compounds before and after cooling in liquid air was observed to be as follows :

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[1] Other observers have found this compound to become yellow in boiling oxygen.

Substance.	Color at ordinary temperatures.	Color at the temperature of liquid air.
Lead iodide	golden yellow	pale sulphur-yellow
Phosphorus pentabromide	citron-yellow	white, or very pale yellow
Phosphorus heptabromide[1]	red	yellow
Mercuric bromiodide	pale yellow	white
Iodoform	yellow	white, or nearly so
Benzene dibromsulphonanide	orange	pale sulphur-yellow
Tribromphenol bromide	yellow	very pale yellow.
Mercuric iodide	red	orange-yellow

It will be observed that all of these compounds became markedly lighter in color on cooling to —190° C., and in some cases the change of color was most striking. It would seem, therefore, that these results tend to confirm the idea that the color of halogen compounds is due to dissociation.

Before leaving this phase of the subject, it might be well to call attention to an observation by Van 't Hoff. In his "Études de Dynamique Chimique," Eng. Trans., p. 273, he points out that at 60° C. *in vacuo*, silver bromide dissociates in the sense of the equation :

$$2AgBr \rightleftarrows 2Ag + Br_2,$$

and that silver bromide at 60° C. *in vacuo* will decompose until the bromine vapor evolved has reached a pressure of 2.9×10^{-53} mm.

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[1] This compound has hitherto been regarded as the red modification of phosphorus pentabromide. Kastle and Beatty have recently shown, however, that the substance is in reality a higher bromide of phosphorus, probably the heptabromide, PBr_7.

It would seem to be generally, if not universally true, that colored substances become lighter in color on cooling to very low temperatures. That such is the case may be seen from the following :

Substance.	Color at ordinary temperature.	Color at —190°.
Bromine	dark red, opaque	orange-red
Iodine, solid	steel-gray	steel-gray
Iodine, in alcoholic solution	brown	very light yellowish brown
Iodine, in carbon disulphide solution	pink	very light pink
Sulphur, rhombic	sulphur yellow	nearly colorless
Phosphorus, red modification	dark crimson	ferruginous-brown
Copper sulphate	dark blue	dark blue
Chrome alum	dark plum color	pinkish violet
Manganous chloride	pink	very light pink
Chromic chloride	violet	pink
Phenolphthalein (alcoholic solution, alkaline)	pink	colorless
p-Nitrophenol (alcoholic solution, alkaline)	yellow	lighter yellow

At the temperature of liquid air fluorescein and eosin in alkaline alcoholic solutions retained their characteristic colors, but became considerably lighter in tint.

From these few observations it would scarcely be logical to conclude that the lightening of color produced by cooling to very low temperatures is in all cases due to the same cause as that which operates in the case of bromides and iodides. On the other hand, it is an interesting and suggestive fact that any increase in the depth of color produced by rise of temperature is usually accompanied by a corresponding increase in the chemical activity of the substance, and with such facts before one, it is almost impossible to keep out of mind such reversible processes as the following :

$$N_2O_4 \text{ (colorless)} \rightleftarrows 2NO_2 \text{ (reddish-brown)},$$

and

$$2HI \text{ (colorless)} \rightleftarrows H_2 + I_2 \text{ (violet)}.$$

In the light of the electrolytic-dissociation theory regarding the action of indicators, the effect of very low temperatures on the color of an alcoholic solution of phenolphthalein which has been rendered alkaline with caustic soda, is certainly most remarkable and interesting.

There is still another point of interest connected with this subject. This is regarding the effect of very low temperatures on the color of allotropic modifications of the same substance. It is well known that the red modification of mercuric iodide becomes orange-yellow when cooled in liquid oxygen, and that on removal from the bath of liquid oxygen, it quickly changes to red again. By some chemists this has been construed to mean that at very low temperatures the yellow variety of this compound is more stable than at ordinary temperature and that the yellow form of the iodide obtained by great cooling is identical with that produced by heating above 128°.[1] There can be little doubt regarding the correctness of the first of these conclusions, namely, that the yellow modification of mercuric iodide is more stable at these very low than at ordinary temperatures. It has been shown, for example, that at —35° monoclinic sulphur changes to orthorhombic about five hundred times more slowly than at ordinary temperature.[2] To conclude, however, that the yellow form of mercuric iodide obtained by cooling the red to —190° C. is identical with the yellow variety obtained by heating the red to 128° is certainly incorrect, as may be seen from the following:

Small amounts of mercuric iodide were sublimed in test-tubes. These tubes were then allowed to stand until a certain amount of the yellow had changed to red. Both the red and yellow varieties of this compound were thus obtained side by side in the same tube. On placing such tubes in liquid air, it was observed repeatedly that the red variety of the compound became orange-yellow, and that the yellow variety became white, or very pale-yellow. Above the level of the liquid air the yellow modification of the compound retained its ordinary yellow color, thereby rendering these differences in color the more pronounced by contrast. The difference in color between the red and yellow modifications of mercuric iodide at —190° C. was thus rendered plainly visible. The effect, therefore, of these very low temperatures on the red modification of mercuric iodide is not to convert it into the yellow variety stable above 128°, but simply to lighten its color in a manner characteristic of other colored bromides and iodides. Therefore, at all temperatures below 128°, the red and yellow modifications of mercuric iodide are distintly different substances.

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[1] Newth's "Inorganic Chemistry," 5th edition, p. 558.

[2] See also "The Phase Rule," Bancroft, 32-34.

In conclusion, I desire to thank Professors Freer and Simon for their kindness in furnishing the liquid air necessary for these experiments.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, March, 1900.

ON THE SUPPOSED ALLOTROPISM OF PHOSPHORUS PENTABROMIDE.

BY J. H. KASTLE AND L. O. BEATTY.

Phosphorus pentabromide has been described as existing in two forms. One of these is yellow and crystallizes in rhombs; the other is red and crystallizes in long prisms. In the preparation of phosphorus pentabromide by adding bromine in theoretical amount to phosphorus tribromide, both the yellow and red bromides are obtained, the former, however, in much the larger quantity. In the same way both varieties are obtained by crystallizing the compound from low-boiling solvents, such as carbon disulphide, etc., and also by subliming the yellow modification in sealed tubes. It has been stated by Baudrimont[1] that the red variety passes into the yellow by rubbing. Beyond this, however, but little seems to be known concerning these substances. It was in the hope of learning something more concerning them that this investigation was undertaken. Phosphorus pentabromide was prepared by adding gradually the theoretical quantity of bromine to phosphorus tribromide. The resulting product consisting mostly of the yellow compound, but mixed with some little of the red, was then sublimed in sealed tubes. Under these circumstances both varieties of the compound were usually obtained. By subliming at 90° C., in an oil-bath, the yield of the red compound could be considerably increased. The attempt was then made to determine the transition temperature of phosphorus pentabromide without success. On long standing the red compound was observed to change to yellow, but at just what temperature and under exactly what conditions it seemed at first almost impossible to determine. The first thing to furnish a clue to the nature and relation of these two substances was their conduct towards water. When the yellow phosphorus pentabromide is brought in contact with water it can be observed to change to the white oxybromide. This then dissolves in water, and ultimately a colorless solution is obtained. On the other hand, the red bromide dissolves in water apparently without the production of the intermediate oxybromide, and gives a solution which has the color of bromine water. Further, the reddish-yellow color of this solution is permanent. In fact, some of it was heated in a closed tube to 100° C. for several hours without any perceptible alteration in color. On shaking the reddish-yellow solution with carbon disulphide, bromine is removed and a colorless aqueous solution is obtained. It is difficult to see how two allotropic modifications of phosphorus pentabromide could so conduct themselves towards water. It occurred to us, therefore, that about the only way in which to account for a modification of phosphorus pentabromide yielding free bromine on solution in water would be to suppose it to have something of a perbromide nature, such as might possibly be represented by the formula $PBr_3.Br_2$, in which event the compound would also yield phosphorous acid instead of phosphoric acid on decomposition by water. Thus,

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[1] Bull. Soc. Chim. de Paris, 1861, 118.

$$PBr_3.Br_2 + 3H_2O = H_3PO_3 + 3HBr + 2Br,$$

whereas,

$$PBr_5 + H_2O = POBr_3 + 2HBr,$$

and $$POBr_3 + 3H_2O = H_3PO_4 + 3HBr.$$

In order to test this point, small quantities of the red bromide were dissolved in water. The cold solution thus obtained was shaken with a small amount of zinc dust, in order to remove free bromine. It was then filtered, and the colorless filtrate tested for phosphorous acid by the phosphine test, and also by warming some of it with mercuric chloride. In neither case was any evidence of phosphorous acid obtained. It then occurred to us that the red substance might possibly be a higher bromide of phosphorus than the pentabromide. That this is the case would seem to derive support from the following facts: First, heat is evolved when bromine is added to phosphorus pentabromide; secondly, on adding a very small quantity of phosphorus tribromide to the red compound, the latter changes to the yellow pentabromide. This change takes place slowly, even in the cold, and very rapidly on warming; thirdly, in contact with bromine vapor, crystals of pure phosphorus pentabromide are changed to the red compound with absorption of bromine; fourthly, on sublimation, especially at 90° C., the crude phosphorus pentabromide gives a sublimate consisting of both the yellow and red compounds, and a small quantity of liquid, probably phosphorus tribromide, is often seen in the bottom of the tubes. On the other hand, the yellow crystals of phosphorus pentabromide which have been purified by sublimation, yield chiefly the yellow compound on resublimation in sealed tubes. Small quantities of the red compound, however, have always been obtained, along with the yellow, under all circumstances. On the other hand, the red compound has been found to yield chiefly red crystals on resublimation, only a few of the yellow crystals being obtained towards the end of the process. On the supposition that a higher bromide of phosphorus, such as the heptabromide, really exists, these changes become readily intelligible. First, the reaction

$$PBr_5 + 2Br = PBr_7$$

would probably be exothermic; secondly, the formation of a higher red bromide of phosphorus would explain the change of color produced by the action of bromine on the yellow phosphorus pentabromide,

$$PBr_5 + 2Br = PBr_7,$$

and, conversely, if phosphorus tribromide were to act upon phosphorus heptabromide, it would be natural to suppose that phosphorus pentabromide would be formed. Thus :

$$PBr_7 + PBr_3 = 2PBr_5.$$

This would account for the change from red to yellow on adding a small quantity of phosphorus tribromide to the red compound. Fourthly, from its mode of formation from phosphorus tribromide and bromine, crude phosphorus pentabromide might be expected to consist largely of the pentabromide, together with smaller amounts of a higher bromide, such as phosphorus heptabromide, and also phosphorus tribromide. On subliming such a mixture in sealed tubes, a separation of these constituents might be effected. Such, indeed, has been observed to be the case. Then again, phosphorus pentabromide and phosphorus heptabromide both undergo dissociation readily when heated. Hence, such changes as the following would be possible, even on subliming the pure compounds :

$$PBr_5 = PBr_3 + 2Br,$$

and

$$PBr_5 + 2Br = PBr_7,$$

and in case of the red compound,

$$PBr_7 = PBr_5 + 2Br.$$

These facts would certainly seem to indicate the existence of a higher bromide of phosphorus having a red color. The attempt, therefore, has been made to isolate this higher bromide in a state of purity. A small quantity of phosphorus pentabromide, together with the theoretical amount of bromine to form phosphorus heptabromide, were heated in a sealed tube. On keeping this mixture at 90° for some time, a sublimate consisting of prismatic red crystals was obtained. This compound gave the following numbers on analysis :

	Calculated for PBr_7.	Found.
P	5.25	5.40
Br	94.75	96.20
Total	100.00	101.60

Considering the difficulties in the way of handling the compound, it will be observed that these figures agree fairly well with those required by the theory for phosphorus heptabromide. Phosphorus heptabromide has usually been obtained in the form of bright-red, transparent, prismatic crystals. Under some circumstances it has been found to resemble chromium trioxide, or arsenic triiodide in general appearance. It is very unstable and seems to undergo dissociation even at ordinary temperatures. Hence, it is best preserved in sealed tubes. On standing in contact with bromine absorbents, it gradually loses its red color and passes to the yellow pentabromide. On rubbing, it also loses bromine and becomes yellow. This would explain the apparent change of the allotropic red modification of phosphorus pentabromide into the yellow, as described by Baudrimont. In our work on this substance we have seen certain indications of still other higher bromides of phosphorus. It is our intention to investigate these substances more fully.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, April, 1900.

Contribution from the Chemical Laboratory of Hobart College.

ON THE ACTION OF NITROUS ACID ON ETHYL ANILINOMALONATE.

[PRELIMINARY REPORT.]

BY RICHARD SYDNEY CURTISS.

In a former paper[1] I described a peculiar oxidation of ethyl anilinomalonate, which was effected by treating the substance dissolved in ligroin with mercuric oxide. This resulted in the formation of ethyl dianilinomalonate. This same change can be brought about with other oxidizing agents. The mechanism of this reaction I will report upon later.

Of especial interest is the behavior of ethyl anilinomalonate with nitrous acid. I will give a brief account, at this time, of experiments now under way, in order to be allowed to continue this line of research undisturbed, and will report results in full in this JOURNAL in the near future.

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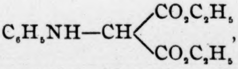
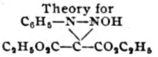
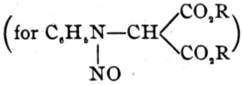
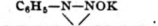
[1] This JOURNAL, 19, 691.

If ethyl anilinomalonate,  $C_6H_5NH{-}CH\left\langle\begin{matrix}CO_2C_2H_5\\ CO_2C_2H_5\end{matrix}\right.$, in suspension in water, is carefully treated with sodium nitrite and sulphuric acid, a thick, clear, amber-colored oil is obtained.

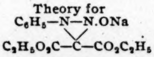
A molecular weight determination made with a carefully prepared sample of the oil gives, by the freezing-point method, in pure benzene :

	Molecular weight found.	Theory for  $\begin{matrix}C_6H_5{-}N{-}NOH\\ \diagdown\diagup\\ C_2H_5O_2C{-}C{-}CO_2C_2H_5\end{matrix}$
(1) 1st det.	259	280
(1) 2nd det.	264	
(1) 3rd det.	268	
(2) 1st det.	253	

This body is extremely unstable, and, if not carefully freed from traces of impurity, it quickly dissociates on standing, even by contact with traces of pipe-water residue on the flask, or with bits of broken glass. Even when pure it loses nitric oxide gas on standing in the sunlight, or when slightly warmed. It does not give Liebermann's nitroso reaction  $\left(\text{for } \begin{matrix}C_6H_5N{-}CH\\ |\\ NO\end{matrix}\left\langle\begin{matrix}CO_2R\\ CO_2R\end{matrix}\right.\right)$. It has, moreover, marked acid properties, giving a well-crystallized, but unstable, sulphur-yellow potassium salt when treated with a solution of potassium hydrate. This salt decomposes near 118° with evolution of gas.

	Theory for  $\begin{matrix}C_6H_5{-}N{-}NOK\\ \diagdown\diagup\\ C_2H_5O_2C{-}C{-}CO_2C_2H_5\end{matrix}$	Found.
K	12.26	11.60

Sodium hydrate yields an equally well defined and unstable canary-yellow sodium salt, which decomposes, when quickly heated, at 118°–122° with evolution of gas.

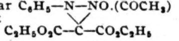
	Theory for  $\begin{matrix}C_6H_5{-}N{-}N.ONa\\ \diagdown\diagup\\ C_2H_5O_2C{-}C{-}CO_2C_2H_5\end{matrix}$	Found.
Na	7.28	7.41

From the sodium salt an insoluble white silver salt can be made with silver nitrate. The clear, yellow, aqueous solutions of the sodium and potassium salts decompose, even in the cold, in an hour or two, and a clear yellow oil separates, having a marked odor like an isonitrile. From this oily emulsion, white needles separate in a few days.

Metallic sodium gives a light-yellow sodium salt with evolution of hydrogen. A solution of sodium carbonate is quickly colored yellow but appears to act but slightly on the oil. Ammonium hydrate gives a still less stable crystalline salt, which is entirely decomposed to ammonia and a clear yellow oil at 35°–37° in ether solution.

Ferric chloride, in alcoholic solution of the acid oil, gives a deep-red color. Concentrated mineral acids turn it red. Sulphuric acid liberates oxides of nitrogen. Hot concentrated hydrochloric acid causes an evolution of gas and gives a marked odor of phenol.

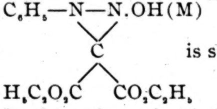
Treated with acetic anhydride at 100°–140°, 4 grams of the clear amber oil gave 1 gram of white needles (m. p. 114°); 2–3 grams of clear, neutral, thick oil, and 120 cc. of a colorless gas, which is in large part nitric oxide, turning red in the air with formation of nitrogen peroxide. A molecular weight determination made with this body (constant m. p. 114°) gave in pure benzene by Beckmann's boiling-point method :

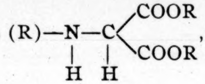
	Substance. Gram.	Molecular weight found.	Molecular weight for  $C_2H_5O_2C{-}\overset{C_6H_5{-}N{-}NO.(COCH_3)}{C}{-}CO_2C_2H_5$
1st det.	0.0593	264	322
2nd det.	0.1003	334	
3rd det.	0.1383	346	

Operating in apparently the same way on another sample of the oil, a crystalline body was obtained of constant m. p. 111° on recrystallization from alcohol, and none of the 114° m. p. crystals. The average of four closely agreeing molecular weight determinations made with this substance (m. p. 111°) gave 222 as the molecular weight found.

These two neutral products, obtained by the action of acetic anhydride are quite stable, decomposing near 200°.

Reduction of the acid oil in dilute alcoholic solution by sodium amalgam results in loss of nitrogen in the form of ammonia and formation of a small amount of an orange-colored crystallized body. As a quantity remained, insufficient for analysis, of the substances on which the molecular weight determinations were made, no definite conclusions are drawn from the above results at this time.

The formula  is suggested as possibly the correct one for the amber-colored oil and its salts.

I shall make a thorough study of this interesting substance and its derivatives, as well as of the behavior of other negatively substituted derivatives , with oxidizing agents, and report the results in this JOURNAL.

HOBART COLLEGE, GENEVA, N. Y.,
April 18, 1900.

ON A MINIMUM IN THE MOLECULAR LOWERING OF THE FREEZING-POINT OF WATER, PRODUCED BY CERTAIN ACIDS AND SALTS.

BY VICTOR J. CHAMBERS AND JOSEPH C. W. FRAZER.

The molecular lowering of the freezing-point of water by dissolved substances, would be expected to remain constant as with non-electrolytes, or to increase with increase in dilution as with electrolytes. With non-electrolytes the molecular lowering does remain very nearly constant with increase in the dilution of the solution, after a certain dilution is reached, but it has long been known[1] that the molecular lowering of substances like cane sugar increases very considerably with increase in concentration from a certain point. In a word, there is a well-defined minimum in the molecular lowering produced by such substances.

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[1] Arrhenius: Ztschr. phys. Chem., **2**, 495; Jones: *Ibid.*, **12**, 642.

In the case of electrolytes, there were, until very recently, but few substances[1] with which such a minimum was suspected. Jones and Chambers[2] have, however, pointed out a number of substances in which a minimum in the molecular lowering of the freezing-point undoubtedly exists. They studied in this connection the chlorides and bromides of magnesium, calcium, strontium, and barium, and plotted the results obtained in curves. These showed very clearly the presence of the minimum in the molecular lowering, and this minimum occurred for the different compounds at approximately the same dilution—from one-tenth to two-tenths normal.

The conductivities of the same solutions of these compounds were measured and the results likewise plotted in curves. The conductivity curves, unlike the freezing-point curves, were perfectly regular, showing no sign of any minimum at any concentration. The dissociation of these substances thus continued to increase with increase in dilution, with perfect regularity, as is shown by the regular increase in the conductivity. Taking into account all of these facts, and, further, that the chlorides and bromides of the alkaline earths are, in general, very hygroscopic substances, Jones and Chambers offered the following suggestion as a possible explanation of the abnormally great lowering of freezing-point produced by the above compounds in concentrated solutions. "In concentrated solutions these chlorides and bromides must take up a part of the water forming complex compounds with it, and thus removing it from the field of action as far as freezing-point lowering is concerned. The compound, which is probably very unstable, formed by the union of a molecule of the chloride or bromide with a large number of molecules of water, acts as a unit or as one molecule in lowering the freezing-point of the remaining water. But the total amount of water present, which is now acting as solvent, is diminished by the amount taken up by the chloride or bromide molecules. The lowering of the freezing-point is thus abnormally great, because a part of the water is no longer present as solvent, but is in combination with the chloride or bromide molecules.

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[1] Arrhenius: Ztschr. phys. Chem., **2**, 496.

[2] This JOURNAL, **23**, 89.

But the conductivity results must also be taken into account. These show, unmistakably, a marked degree of dissociation even in the most concentrated solutions employed. There must, therefore, be a certain number of the molecules broken down into ions, either by the water acting as solvent or by the water in combination with the molecules, just as salts are probably dissociated in their water of crystallization.''

Jones and Chambers point out, further, that there are unquestionably hygroscopic substances known which combine with water in concentrated solution. This is especially true in the case of sulphuric acid, where well-defined compounds are known.

The object of the present investigation is to study other hygroscopic substances, to see whether very different classes of compounds show this abnormally great freezing-point lowering in concentrated solutions. The compounds with which we have worked are hydrochloric acid, phosphoric acid, sodium acetate, zinc chloride, strontium iodide, cadmium iodide, and copper sulphate. These substances were purified by the methods best adapted to each case, and solutions prepared and standardized. In standardizing the solutions that constituent was chosen which could be most accurately and readily determined. From the standard solution the remaining dilutions in each case were directly prepared.

The method employed in measuring the freezing-point lowering was essentially the Beckmann method. We were careful to keep the temperature of the freezing-bath only a little below the freezing-temperature of the solution. The results which we obtained are given in the following tables. Column I gives the concentration in terms of normal, column II the freezing-point lowering observed, column III the correction to be introduced for the separation of ice, which concentrates the solution, column IV the corrected freezing-point lowering, and column V the molecular lowering of the freezing-point:

Table I.

$CuSO_4$.

I.	II.	III.	IV.	V.
0.476	0°.722	0°.008	0°.714	1.50
0.595	0°.885	0°.019	0°.866	1.45
0.890	1°.300	0°.025	1°.275	1.43
1.190	1.°795	0°.055	1°.740	1.46

Table II.

H_3PO_4.

I.	II.	III.	IV.	V.
0.118	0°.282	0°.008	0°.274	2.32
0.236	0°.545	0°.010	0°.535	2.26
0.472	1°.065	0°.026	1°.039	2.20
0.944	2°.176	0°.033	2°.143	2.27
1.41	3°.410	0°.061	3°.349	2.37
1.62	4°.270	0°.057	4°.213	2.60

Table III.

HCl.

I.	II.	III.	IV.	V.
0.051	0°.187	0°.002	0°.185	3.63
0.102	0°.360	0°.007	0°.353	3.46
0.204	0°.755	0°.010	0°.745	3.65
0.408	1°.565	0°.030	1°.535	3.76
0.516	2°.003	0°.047	1°.956	3.79
1.032	4°.330	0°.092	4°.238	4.10

Table IV.

CH_3COONa.

I.	II.	III.	IV.	V.
0.058	0°.216	0°.005	0°.211	3.64
0.116	0°.421	0°.008	0°.413	3.55
0.174	0°.650	0°.022	0°.628	3.61
0.232	0°.861	0°.016	0°.845	3.64
0.348	1°.312	0°.033	1°.279	3.67
0.464	1°.774	0°.038	1°.736	3.74

Table V.

CdI_2.

I.	II.	III.	IV.	V.
0.133	0°.315	0°.001	0°.314	2.36
0.222	0°.480	0°.001	0°.479	2.16
0.333	0°.720	0°.010	0°.710	2.13
0.444	1°.005	0°.008	0°.997	2.24
0.666	1°.575	0°.011	1°.564	2.35
0.888	2°.245	0°.018	2°.227	2.51

Table VI.

SrI_2.

I.	II.	III.	IV.	V.
0.027	0°.143	0°.003	0°.140	5.18
0.054	0°.280	0°.005	0°.275	5.09
0.081	0°.425	0°.010	0°.415	5.12
0.108	0°.572	0°.014	0°.558	5.17
0.162	0°.863	0°.019	0°.844	5.21
0.216	1°.180	0°.024	1°.156	5.35
0.327	1°.855	0°.051	1°.804	5.51

Table VII.

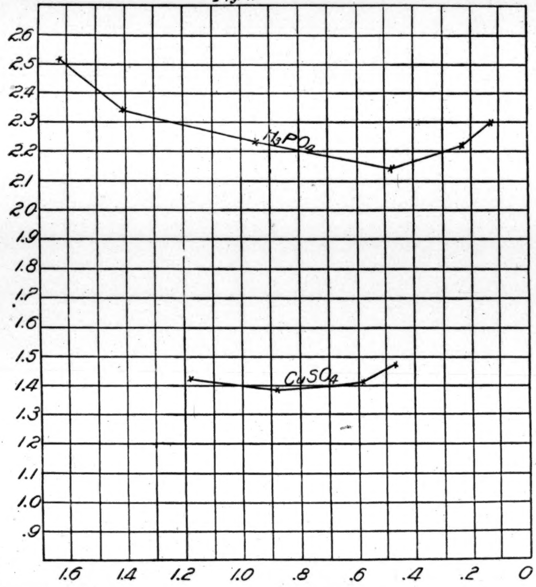
$ZnCl_2$.

I.	II.	III.	IV.	V.
0.0493	0°.270	0.°007	0°.263	5.33
0.0986	0°.521	0.°012	0°.509	5.16
0.197	1°.045	0.°025	1°.020	5.17
0.296	1°.585	0.°042	1°.543	5.21
0.394	2°.138	0.°040	2°.098	5.32
0.592	3°.272	0.°051	3°.221	5.44

These results are plotted in curves (Figs. I-III). The abscissae are concentrations, the ordinates molecular lowerings of the freezing-point. The more dilute solutions were not investigated in this work, since it is well known from previous work that the molecular lowering increases with the dilution in dilute solutions. We have, therefore, carried our measurements only a little beyond the minimum in the molecular lowering.

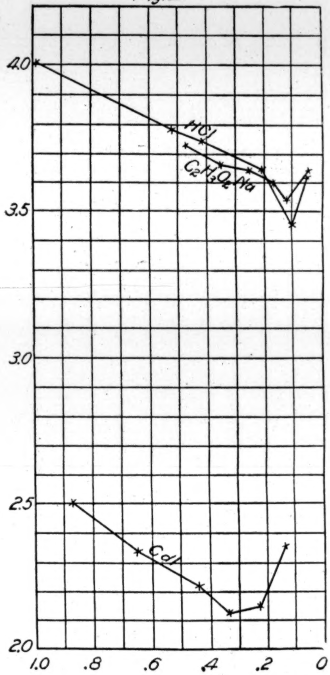
There is no very pronounced minimum in the case of copper sulphate, but the minimum for phosphoric acid comes out very sharply at about five-tenths normal. The minimum appears for hydrochloric acid and sodium acetate between one-tenth and two-tenths normal, while for cadmium iodide it exists at a slightly greater concentration. The minimum occurs for strontium iodide and zinc chloride in the region of a one-tenth normal solution.

Fig. 1.



In all the cases above described, with the possible exception of copper sulphate, there is an unmistakable minimum in the molecular lowering of the freezing-point, and from this minimum the molecular lowering increases with increase in concentration. Nearly all of these substances have a considerable attraction for water. This is shown by a number of these substances in the strong tendency to unite with water when

Fig. II.

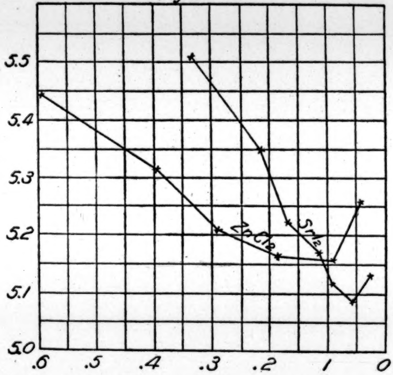


they have been freed from it. This is especially true with hydrochloric and phosphoric acids, and sodium acetate and zinc chloride. In other cases, as with copper sulphate, the attraction for water expresses itself in the water of crystallization in the salt.

We attempted to study disodium phosphate in the same way that we have investigated the above salts, but we were compelled to abandon the attempt because of the comparative insolubility of this compound at low temperatures.

It seems from the above results that the suggestion of Jones and Chambers to account for the minimum in the molecular

Fig. III.



lowering of the freezing-point of water produced by a number of electrolytes, is in the main substantiated by the facts. Indeed, it seems to be the only explanation possible up to the present, if we take into account both the freezing-point lowering and conductivity of these concentrated solutions. At present we seem forced to the conclusion, that in the very concentrated solutions of certain electrolytes there is some kind of union between the molecules of the dissolved substance and of the solvent. This view put forward by Jones and Chambers to account for the abnormal freezing-point lowerings which they had discovered, should be carefully distinguished from the attempt which was made a few years ago to account for all solutions on the basis of a combination taking place between the solvent and the dissolved substance. This latter view was meant to apply to all solutions, dilute as well as concentrated. In dilute solutions we have not the slightest reason to suppose that there is any union between the solvent and dissolved substance, but, on the contrary, the very best evidence that no such union exists. In this connection we have but to refer to the fact that dissociation, as measured by the freezing-point method, agrees with dissociation as measured by the conductivity method; or to the general applicability of the law of Kohlrausch to all solutions of all electrolytes.

Whether the view of Jones and Chambers should prove to be the final expression of the truth, in connection with concentrated solutions of electrolytes which show a minimum in the molecular lowering of the freezing-point, can be decided only by further work. But it is quite certain that any general theory of solutions must take into account such results as those previously described by Jones and Chambers,[1] and as recorded in this paper.

It was early pointed out that the laws of gas pressure do not apply to the osmotic pressure of concentrated solutions, and for this reason, if for no other, comparatively little progress has been made in the study of concentrated solutions from the physical-chemical standpoint. It seems to us quite possible that work of the kind here described may help, if only a little, towards the understanding of concentrated solutions, and we may thus be able to find out why it is that the laws which obtain for dilute solutions do not hold in the more concentrated. It is with this hope in mind that further work along the above line will be done.

In conclusion we wish to express our thanks to Dr. H. C. Jones, at whose suggestion the above investigation was undertaken, and under whose guidance it has been carried out.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
January, 1900.

REPORT.

The Year's Advance in Technical Chemistry.

The year just passed has been perhaps the most important of the whole century in the advance made in all manufacturing industries, especially those having a chemical basis. This advance has been brought about, in a few instances, by the application of radically new methods, but more often by a wonderful enlargement of the scale of operations of well-tried processes, and by the general introduction of automatic mechanical devices and labor-saving machinery. Everywhere the striving for increased tonnage and for getting the very largest possible yield out of each piece of apparatus employed, has been more intense than ever before.

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[1] *Loc. cit.*

Considering first the industry which is of greatest commercial and economical importance in the United States, the metallurgy of iron and steel, the most striking change is the practical doubling in capacity of most of the newly designed blast-furnaces. The daily output of the coming furnace must approach 600 tons of pig-metal, while the maximum for most furnaces heretofore has been a daily average of from 200–300 tons. When we consider that only a decade ago an output of 100–150 tons daily was considered good practice, we can appreciate the magnitude of the change and wonder where the limit of the future is to be. The greater part of this increase has been caused by doubling, or more than doubling, blast pressures and blast quantity, thereby increasing the yield of existing furnaces and rendering possible larger hearth diameters.

A considerable increase of economy in the use of fuel for making pig-iron seems to have been accomplished abroad by the direct use of furnace gases in gas-motors for producing the air-blast, instead of burning this gas to generate steam and using steam-engines to operate the blast pumps. The solution of this problem is cause for congratulation, because of the numerous difficulties connected with it. The gas from iron-furnaces available for such motors contains only about 25 per cent of carbonic oxide, as almost its whole source of heat value, besides carrying large quantities of fine dust of coke, ore, etc., which greatly increases the difficulty of use in any mechanism where corrosion must be avoided. Any one who has seen the valves of a hot-blast stove cut through and worn out in a few months by the action of this dust will appreciate its cutting power.

In Scotland, furnaces using raw coal have made as a by-product about a tenth of all the ammonia produced in Great Britain during the year. Certain localities in the United States possessing abundant non-coking coal in proximity to cheap and good ore, might profitably adopt this method of iron manufacture, notably the new Michigan coal district of the Saginaw Valley, which, by this means, could easily supply the whole of the iron used in Michigan districts and all of the ammonia needed in the newly developing alkali industries of that locality.

Another important factor in the great increase of furnace capacity for the production of pig-iron has been the installation of automatic labor-saving devices for handling furnace-charges and removing furnace products. The most important of these are the car and ore-loading machines of Brown, McMyler, Lindsey, and Hulett, the casting machine of Uehling for handling the metal, and the various methods for carrying charges to the furnace top, with automatic dumping and distributing devices. These latter have removed the necessity for charging men or any laborers continuously at the charging level, where the work is exhausting and dangerous. By the use of a double bell they effect a thorough mixture of the charge and prevent the loss of furnace-gases.

The successful conversion of blast-furnace slag into a fair quality of hydraulic cement at a number of furnaces is a long step toward the economical solution of the troublesome problem of the disposal of this vast by-product. It has been found that certain grades of basic slag in which the proportion of magnesia and sulphur is not too high, by simply being granulated with water as they flow from the furnace, ground extremely fine and intimately mixed with the proper proportion of lime, are converted into a hydraulic cement which forms a cheap and, under certain conditions, an excellent substitute for Portland cement, and for which a permanent demand has been created.

In the production of steel the gap between the cost of producing Bessemer and open-hearth metal has been further lessened, mainly by the general introduction of basic open-hearth furnaces of greatly increased capacity and of labor-saving devices in charging metal and fluxes. Most important of these latter is the charging machine of Wellman. In this connection, too, the large introduction of the Wellman tilting open-hearth furnace during 1899 is worthy of mention, and a probable further economy of operation will be secured by their use. Several large plants using these tilting furnaces have been installed during the past year, and, while they have been used in a number of places heretofore, the record of their efficiency has not as yet been made public and is awaited with great interest. While their cost of construction is about 25 per cent more than that of the older stationary type, the complete removal of all metal and slag from the furnace hearth at each operation, with the resulting saving of metal, the saving of the time necessary for tapping, the small amount of repair necessary to the bed after the removal of each charge, and the facility with which this can be accomplished are factors which will probably cause this to become the standard type of steel furnace of this decade.

In Bessemer practice the most noticeable improvement is the general introduction of the Jones mixer for receiving the molten pig-metal direct from the furnace, thus saving its contained heat and doing away with cupolas for melting the iron previous to its treatment in the converter. This method effects not only a saving in heat or fuel, but a greater gain in the cost of handling the iron. It has been found that only about one laborer in a hundred can endure the strain of continuously handling the heavy pigs of metal at the blast-furnace in their removal from the sand molds and loading on cars. The doing away with this severe labor by the direct use of hot metal in the Bessemer plant and by the use of the Uehling casting machine seems, therefore, a gain to humanity as well as in the money value saved. The basic converter still fails to gain a permanent foothold in this country, and, because of our immense deposits of pure ore and beds of phosphate rock, and of the continued encroachments of the open-hearth process, probably never will.

The metallurgy of copper has undergone changes similar to those of iron, only in a much smaller degree. The most important of these are the increased use of the Bessemer converter in refining mattes, and an increased output of electrolytically refined metal. The general use of a gold-bearing material as a lining for the converter in matte Bessemerizing has effected a material economy. In roasters for copper sulphide ores, several new devices have gained general use. A Denver-made modification of the old Spence furnace, with its numerous beds and automatic plow rakes, in which the operating chains are placed upon the exterior of the hearth, and the Herreshoff furnace, consisting of a vertical cylinder with horizontal diaphragms or beds and rakes operated by a central shaft, have perhaps received the largest installment during the year. A plant of considerable size to operate the Hoepfner process of refining copper has been in operation for some time, but reliable cost data are not at hand. This process depends upon dissolving the oxidized metals with cupric chloride and electrolyzing the chloride solution. The process was tried at the Brooklyn experimental plant of a copper-nickel refining company some years ago, but was abandoned.

In the metallurgy of nickel the principal event has been the installation in England of a considerable plant to use the Mond process of refining by carbonic oxide, and of a plant in this country utilizing a new but unpublished process. Storer's method proposed, but not yet installed on a commercial basis, applies the old Hunt and Douglass copper method to nickel ores, treating nickel oxide at high temperature with a strong solution of ferrous chloride.

In the treatment of lead, tin, silver, mercury, and zinc ores, changes during the year seem to have been unimportant. Several methods have been proposed for treating the low-grade argentiferous blende-galena ores, so common in Colorado, but none has as yet stood the test of successful commercial application.

The output of gold has been further increased by the installation of many new cyanide works, much of the material treated in these mills being the tailings from old amalgamation plants or of abandoned dump heaps. Electrolyzing the cyanide solutions in this process is becoming more common. The Sulman-Teed method of adding a small quantity of cyanogen bromide to the lixiviating solution is claimed to effect increased gold extraction, especially in arsenic-bearing ores, but it is also asserted by many that the loss of cyanogen by this method is too great for success, and more time must be allowed for further evidence. A method of assisting the free access of the oxygen probably necessary to the solution of gold by cyanide solutions, which consists in violently agitating the ore with the solution by means of air introduced into the mixture under considerable pressure has been patented and is now being largely advertised under the name of the "Pneumatic Process." A possible serious objection to the use of this method is that an increased loss of cyanide may occur from excessive oxidation and decomposition by carbonic dioxide. During the years immediately following the marked success of the cyanide process in South Africa, the tendency was to introduce this method for all sorts of ores and under all sorts of conditions, whether adapted to success in this way or not. Now, the proper limitations of the use of cyanide solutions are better understood, and the chlorination process is again receiving more attention, so that the two methods are now beginning to assume their proper and normal relation to each other. Increasing amounts of gold and silver are being recovered by matting the ores with copper- and sulphur-bearing material, Bessemerizing this matte to blister copper, and electrolyzing the product.

In several industries the year has been marked by the beginning of that vast shifting of location from coal to water-power situations, which is to mark the coming decade. In several cases this shifting has already been nearly completed, notably in the production of chlorate. Norway, Scotland, Switzerland, and the mountain regions of France and the United States, where water-falls abound, are destined to become centers of manufacturing activities fully as great in many industries as the older coal localities, and with the advantage, that the coal fields once exhausted are gone forever, while water powers last for all time. This recent great development of the uses of water-power is due to new electrolytic processes, to material improvements in the transmission of hightension currents, to improvements of dynamos, and to the development of water-turbines to utilize extreme pressures. This transference of many old industries to water-power districts will be limited only by the cost of carriage of the raw material to the plant, and of the finished product to its market. The competition with coal-generated power thus occasioned must result in a more and more economical use of fuel, and the year has shown material progress here. The previously mentioned use of blast-furnace gases in gas-motors is of this nature, but the very large year's increase of by-product coke-oven plants is of greater significance. In America new ovens of the Semet-Solvay or the Hoffman type have been started during the year at Halifax, Boston, Glassport, Pa., Benwood, W. Va., and Ensley, Ala. This is a satisfactory improvement, because the wasteful use of coal in bee-hive ovens will always remain a reproach of the 19th century, especially in American and English practice. These by-product coke ovens effect an increase of from 10 to 15 per cent in the amount of coke produced, with a saving of 3–4 per cent of the weight of coal tar, 0.4–0.8 per cent ammonium sulphate, and 7–10 per cent gas in excess of that required for coking. These last three items almost equal in value the coke produced.

The skill and care required in operating the Mond gas-producer, considerable fluctuations in the price of tar and ammonia, and the high cost of construction and depreciation of plant have restricted the introduction of this most valuable invention to a few localities, but a number of such plants have been started during the year and with considerable success. Probably the most important progress in the use of fuel and our greatest present hope of delivery from the smoke domination in soft coal districts, lies in the success of the Dellwick water-gas process which the past year has shown. In this device the fuel is burned directly to carbonic dioxide during the heating, or air-blast period, by using extra high blast pressure, and skillfully distributing its contact with the fuel. This increases the gas yield by nearly 100 per cent, and reduces the total loss of the heat value of the fuel from 55 to only 18 per cent. During the past year a plant has been installed in Pittsburg for the conversion of coal into fuel gas, utilizing a radically new method, which also bids fair to solve this important fuel question, and the result of this experiment is awaited with intense interest.

In many instances, where petroleum has been used as fuel, its recent increased cost has forced its abandonment. This has made the discovery of an equally convenient and efficient fuel a great desideratum. Fortunately such a substitute for oil has been found in the use of finely-powdered bituminous coal, injected into the furnace with an air-blast just as oil is used. The coal is thoroughly dried and ground very fine. Its only drawback seems to be almost explosive combustibility, rendering its storage unsafe. The temperature attainable by this means seems to be almost equal to that with oil, and in respect to cost and some other considerations it is more advantageous.

During the year a wonderful growth in the manufacture of Portland cement has taken place in the United States, so that within the coming decade we may reasonably expect to supply all of the home consumption and probably a great part of that used in other countries. The principal improvement in methods has been the general introduction of the automatic rotary kiln or burning furnace. These consist of inclined steel cylindrical shells about 60 feet long, mounted on rolls and lined with magnesia brick. The cement mixture is pumped with water or fed dry by a screw into the upper end and falls out as burned clinkers continuously at the lower end. The fuel used is oil, gas, or powdered coal, the process is continuous and requires a minimum of manual labor. The success of this invention, which has been brought about commercially in the United States first, has been so pronounced that American experts have been called to the oldest and best cement-producing districts in the world, to reconstruct their plants on the new lines.

In the manufacture of sulphuric acid, 1899 has seen the successful beginning of the greatest revolution since this acid began to be produced on a large scale, namely, the production of sulphuric trioxide, SO_3, by the contact power of finely-divided platinum on a mixture of sulphurous oxide and air. This reaction was long ago discovered by Winkler and utilized for making dry sulphuric trioxide and fuming acid, but the heat produced soon checked the reaction, and the converting power of the platinum soon gave out. The experts of the Badische Anilin and Soda Mfg. Co., a few years ago discovered the cause of the latter trouble to be the presence of dust and foreign gases, principally arsenic and phosphorus compounds, and much moisture. By using purified gas and providing a way of escape for the excess of heat generated by the reaction, the process became quantitative, even with dilute sulphurous anhydride and hence commercially possible for making all kinds of sulphuric acid. Many German acid makers are reported to be rapidly eliminating their lead chambers and using platinized asbestos or pumice-stone instead. The new method is especially economical for the strongest acids, the stronger the acid to be made the greater the economy over the niter method. Weaker acids, up to chamber acid strength, are probably still made much more cheaply by present methods. The new process is best also for making the purer grades, for, by using pure sulphurous gas, chemically pure acid can be made as cheaply as any other.

The latest antagonist by which the old salt-cake and muriatic acid soda and bleach industry has been assailed, namely, the electrolytic process of chlorine and soda production, has, during the past year, developed into such a giant that, with its older competitor, the ammonia-soda process ever enlarging, the death of the LeBlanc process cannot be postponed many years. Only in Great Britain does the process, by virtue of the retaining energy of immense capital invested, survive to any considerable extent. On the European continent ammonia soda had practically expelled it without the assistance of electrolytic methods. In this country it never had a foothold. In England it has survived mainly because of the profit on the chlorine industries. Now, electrolytic methods have removed this last prop, producing bleach as cheaply as the value of the hydrochloric acid used in the older processes. No competition is really ever likely to exist between the ammonia soda and electrolytic processes, because the soda produced by electrolysis is of little worth compared with the value of the halogen. The electrolytic production from salt of all the bleach used would produce only an eighth of the soda required for the world's consumption. There is even some possibility that hydrochloric acid may be made eventually by uniting electrolytic chlorine and hydrogen. The principal electrolytic processes so far successfully installed are the Kastner-Kellner mercury method with large plants at Niagara Falls and in England, the Hargreaves-Bird process using an asbestos diaphragm, with a considerable plant at Liverpool, and the large works at Leopoldschall. The plant at Rumford Falls, Maine, using platinum electrodes, went out of operation during the year. Probably the momentum of large capital invested in the chamber-acid plants and in the LeBlanc soda process will maintain for both a more or less profitable existence for a number of years to come, in spite of all competition.

The great change in the chlorate industry has already been referred to. Practically all that in use is now made by electrolysis. There has been a marked decrease during the year in American imports of chlorate, soda and caustic, due to the installation of large ammonia-soda works at Syracuse, Detroit, and Bay City, and another large works is now under construction at Barberton.

The manufacture of calcium carbide has grown during the year to immense proportions, but with a maintenance of prices, showing a large increase in its use. In Germany nearly all of the railway coaches are now lighted by a mixture of one-third acetylene and two-thirds Pintsch gas, resulting in both an increase of light and decrease of cost.

Another product of the electrical arc furnace which has been largely manufactured during the past year and has found an even larger demand, is graphitized electrolytic carbons. It is found that when ordinary pressed carbons are packed in charcoal and placed in the path of a large electrical current so as to be intensely heated for a considerable time, the carbon of which they are composed is practically converted into graphite. Such graphitized carbons, owing to the uniform texture which they are given, and to the higher power to resist oxidation, are found to have two or three times the life of ordinary carbons for all electrolytic purposes, and their use is rapidly growing.

In the manufacture of wood spirits a greater purity of product has been brought about by greater care in fractioning. Also many new externally heated retort plants are replacing old kiln-furnaces with internal firing for making charcoal, and greater economy is being attained in acetate production.

In the way of rubber products, the new substitute, Reid's "velvril" is claimed to have had a successful year's trial in England, and to have gained a large use. Velvril is a drying oil which has been nitrated, mixed by a common solvent with nitrocellulose, and the solvent subsequently removed. Castor oil is said to be used and, after nitration, contains 4–5 per cent of nitrogen. This, with nitrocellulose, forms a clear, homogeneous, rubber-like mass, its hardness being wholly under control by varying the relative proportions of the two ingredients, from a consistency like vulcanite to that of the softest rubber. The article to be made may be shaped from the mixture while softened by a solvent, or formed into shape by high pressure and heat somewhat above 100° C. In spite of its nitrated character, it is not explosive, but burns slowly and quietly. Numerous uses are claimed for the new compound by its inventors, including insulating material, clothing, belting, varnish, paint, enameling of leather, cement for wood, glass, metal, etc., hose and tubing, and even as a modifier of the explosive rate and power of guncotton and nitroglycerin. If only a small proportion of these claims stand the test of continued use, a most valuable discovery has been made and a substance of the widest applicability and use found at an exceedingly opportune time, because of the enormously increased demand for rubber in so many industries.

Not even a few of the inventions and processes described above were actually begun or perfected during 1899, but all for the first time last year stood the test of continued practical use. Inventions almost without number are recorded every year, but it would take an omnipotent judge to select those that are destined to work industrial revolutions, and their description or bare enumeration would be of little interest and less value here. The record given has therefore been confined to those inventions and changes which the year has recorded as of permanent value and which have proved themselves commercially successful.

ALBERT W. SMITH.

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REVIEWS.

THE THEORY OF ELECTROLYTIC DISSOCIATION AND SOME OF ITS APPLICATIONS. By HARRY C. JONES. The Macmillan Co. 1900.

In preparing this little book the author has had particularly those readers in mind who desire to keep in touch with the recent progress of physical chemistry, but who have not the time and opportunity to consult the original literature or larger German treatises on the subject. Until the recent and very timely appearance of Dr. Walker's excellent work on physical chemistry, there has been, in fact, no English source to which the reader could be unqualifiedly referred, so that the present work will be welcome to a large circle of readers. As the author states in his preface, an attempt is made to answer the questions: "What was physical chemistry before the theory of electrolytic dissociation arose? How did the theory arise? Is it true? What is its scientific use?" and the chapters into which the book is divided correspond to the divisions thus indicated.

Chapter I contains an outline of work done prior to 1885, when modern physical chemistry may be said to have had its beginning; all work which in any way touches on the relations between properties of bodies and their composition and their constitution as well as that on thermochemistry and electrochemistry is here considered: and the characteristic feature of the "old physical chemistry"—namely, its empirical inductive nature is pointed out. This chapter, which takes up a quarter of the whole book might, in the opinion of the reviewer, have been considerably abbreviated to advantage.

The second chapter on the origin of the theory of electrolytic dissociation is admirable and is thoroughly enjoyable reading. The essential parts of Pfeffer's, Van't Hoff's, and Arrhenius' epoch-making papers are given in their authors' own words, all being clearly knit together in historical sequence. A feature of this chapter is the introduction of extracts from Van 't Hoff's Berlin lecture in 1894 on "How the Theory of Solutions Arose" which gives the reader a feeling of almost personal acquaintance with the working of this master mind. Chapter III, "Evidence Bearing upon the Theory," is devoted to a discussion of the numerous physical and chemical phenomena which have found a satisfactory explanation in the light of the dissociation theory. The illustrations are numerous and well chosen, but the general impression left on one unacquainted with the history of the theory is that the dissociation theory has been accepted almost without a question and that it will ultimately take its place among the so-called "laws of nature." This seems unfortunate to the reviewer, although himself a warm supporter of the theory; for, while it is unquestionably true that the hypothesis of Arrhenius, and the theory since built upon it as a foundation, has done more than any previous theory to explain the correlated phenomena of physics and chemistry, yet it is equally true that it still fails to account at all for some unquestionable facts and has had, and still has, some weighty opponents. A short chapter on the objections which have been raised to the theory and the arguments with which they have, for the most part, been satisfactorily answered, would have added to the value of the book and not left the reader with the impression that the theory has attained its present position without a struggle.

The concluding chapter is devoted to applications of the theory. The various methods of determining electrolytic dissociation are considered, and also certain applications to biological and toxic problems. Nernst's theory of the voltaic cell, liquid cells, gas batteries, etc., is gone into at considerable length, this being of particular interest to the physicist. The reviewer would point out that the question of the true seat of electromotive force in the voltaic cell was pretty definitely settled prior to the dissociation theory in an admirable paper by Lodge, in 1885, although no satisfactory theory to account for it was given until the appearance of Nernst's paper.

The work before us is a welcome addition to our literature, and will, no doubt, contribute its part in winning new disciples to the present large (in this country at least) following of the Van't Hoff-Ostwald-Arrhenius school.

H. M. GOODWIN.

TRAITÉ ÉLÉMENTAIRE DE MÉCANIQUE CHIMIQUE FONDÉE SUR LA THERMODYNAMIQUE. Par P. DUHEM, Professeur de Physique Théorique a La Faculté des Sciences de Bordeau. Tome IV, Les Mélanges Doubles. Statique Chimique Générale des Systèmes Hétérogènes. Paris, Librairie Scientifique A. Hermann. pp. 381. 1899.

The appearance of the earlier volumes of Duhem's work has already been noticed in this Journal (**19**, 621). The nature of the fourth volume can best be seen from a brief account of its contents. This volume contains two books, 8 and 9. Book 8 deals with double mixtures and is divided into nine chapters. Chapter I, General Theory of Liquid Mixtures; Chapter II, Theory of Distillation; Chapter III, Critical Conditions of a Mixture; Chapter IV, Liquefaction of a Gaseous Mixture; Chapter V, Liquid Double Mixtures; Chapter VI, Gaseous Solutions; Chapter VII, Mixtures of Volatile Liquids; Chapter VIII, Dissociation; and Chapter IX, Isomorphous Mixtures. The amount of material treated in book 8 is very great, indeed, and it will be noticed that it includes much that is usually treated in works on physical chemistry under the head of solutions.

Book 9, on Chemical Statics of Heterogeneous Systems, deals with the general principles of statics at a given pressure, general principles at a given volume, and general theorems of univariant and bivariant systems.

The whole work is written from the mathematical and theoretical standpoint rather than from the experimental and, therefore, appeals only to those who are well advanced in the subjects treated. A larger number of references to the literature might have made the work a little more useful to the investigator. The book is very clear, and will doubtless prove of great service in this important branch of science. H. C. J.

LEÇONS DE CHIMIE PHYSIQUE. PROFESSÉES A L'UNIVERSITÉ DE BERLIN. Par J. H. VAN'T HOFF. Membre de L'Académie des Sciences de Berlin. Professeur ordinaire a L'Université et directeur de L'Institut de Physique de Charlottenbourg. Ouvrage traduit de l'allemand par M. Carvisy, Professeur agrégé au Lycée de Saint-Omer, Deuxième Partie. La Statique Chimique. Paris, Libraire Scientifique A. Hermann. pp. 162. 1899.

The translation of the second part of Van't Hoff's book into French has thus appeared shortly after the German edition. This shows that the work of the great leader in modern physical chemistry is appreciated and valued in France as well as in his adopted country—Germany. The appearance of the first part of this book has already been noticed in this Journal (**20**, p. 610). The second part on chemical statics deals with: I. Molecular Weight and Polymerism, including determination of the molecular weights of rarefied gases, and determination of molecular weights in dilute solutions; II. Molecular Structure (Isomerism, Tautomerism), and as subdivisions, determination of constitution, determination of configuration (stereochemistry) and tautomerism; III. Molecular Grouping (Polymorphism), comprising the laws which govern the reciprocal transformation of polymorphous substances, and molecular grouping properly so-called.

As is well known this work is, in a certain sense, a reproduction of the course of lectures given by Van 't Hoff in the University of Berlin on selected topics in physical chemistry. As far as it goes it contains, of course, what is newest and best in the subjects treated. It cannot, however, be regarded as a systematic and comprehensive text-book, covering the whole field of modern physical chemistry, and it is not adapted to the beginner in this branch of science. For those who are well grounded in the fundamental principles of the subject, this book is invaluable and needs no other recommendation than the name of its author. H. C. J.

ERRATA.

Page 296, line 17 from below, for "ammonia" read "ammonia at —38°."

Page 297, line 8 from above, for "water" read "water at 18°," and for "ammonia" read "ammonia at —38°."

Page 298, line 18 from below, for "a" read "α."

Page 299, lines 3 and 19 from above, for "a" read "α."

Page 306, line 5 from above, insert "or" after "salt."

Page 306, line 15 from below, for "investigators" read "investigations."

Page 306, line 6 from below, for "1856" read "18.56."

Page 307, line 12 from above, insert "coefficient" after "temperature."

Page 452, line 7 from below, for "potassium chloride" read "potassium bromide."